

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Hydrometallurgical Treatment of Neodymium Magnet Waste

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Gothenburg, Sweden 2018

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ISBN: 978-91-7597-826-0

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Doktorsavhandlingar vid Chalmers Tekniska Högskola
Ny serie nr. 4507
ISSN: 0346-718X

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Cover: Neodymium magnet (left) and hydrogen decrepitated neodymium magnet powder (right)

Chalmers Reproservice

Gothenburg, Sweden 2018

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Abstract

Recent decades have seen a considerable increase in the usage of rare-earth elements (REEs) in modern technologies and green energy sources. Recycling of REEs out of end-of-life products and E-scrap has become an alternative to mining them out of primary ores due to their supply risk in some countries and development towards circular economies. Neodymium (NdFeB) magnets are of special interest since they are present in various technological waste streams. They contain considerable amounts of REEs such as Nd, Dy, Pr and some others, for example Gd and Tb, depending on the specific application, making them very attractive for REE-recycling. Apart from REEs, neodymium magnets are made up of around 60% iron, which can pose a challenge in their recycling.

Hydrometallurgical methods such as leaching and solvent extraction are attractive and efficient methods for the recovery of REEs out of NdFeB magnets, albeit with certain drawbacks such as large aqueous and organic waste generation during the process and utilization of some hazardous chemicals. The REEs are normally leached out of the NdFeB magnet waste using strong mineral acids such as HCl, HNO₃ and H₂SO₄ but, despite their excellent leaching properties for REEs out of NdFeB magnets, they pose some risk to the environment because there are still issues with poisonous gas evolution during leaching, regeneration of the used acids, and handling of highly concentrated acids can be a challenge. Furthermore, the extracting agents currently used in the industry for REE-extraction are mostly phosphorus-based and do not follow the CHON principle, meaning it is not possible to incinerate them without either the production of ash or acidic gases.

In this work a comparison of leaching efficiency between the traditionally used mineral acids and organic lixiviants was performed. Magnet powder was successfully leached using fully combustible organic lixiviants (including acetic, citric, maleic, glycolic and ascorbic acid), and new green leaching alternatives were developed. Parameters including acid concentration, leaching time, S/L ratio and temperature were investigated and mitigated. Subsequently, the REEs were selectively extracted from these leachates. For this separation step several phosphorus-based extractants (TBP, D2EHPA, Cyanex 272 and 923) were investigated, alongside TODGA, which follows the CHON principle. The influence of various diluents on the extraction was also studied. It was concluded that REEs can be separated into relatively pure aqueous streams using organic acids instead of mineral acids under certain conditions, while TODGA was efficient at separating REEs from large amounts of Fe in these particular waste streams. A process for the extraction of REEs from organic acids leachates was developed, with promising results.

Keywords: neodymium magnets, rare-earth elements, recycling, leaching, solvent extraction

LIST OF PUBLICATIONS

This thesis is based on the work contained in the following publications and manuscripts:

Paper 1:

Marino Gergoric*, Christophe Ravaux, Britt-Marie Steenari, Fredrik Espegren, Teodora Retegan. Leaching and Recovery of Rare-Earth Elements from Neodymium Magnet Waste using Organic Acids. *Metals*. 2018, 8, 721.

Paper 2:

Marino Gergoric*, Antonin Barrier, Teodora Retegan. Recovery of Rare-Earth Elements from Neodymium Magnet Waste using Glycolic, Maleic and Ascorbic Acid followed by Solvent Extraction. Accepted for publication in *Journal of Sustainable Metallurgy* with minor revisions, 2018.

Paper 3:

Marino Gergoric*, Christian Ekberg, Britt-Marie Steenari, Teodora Retegan. Separation of Heavy Rare-Earth Elements from Light Rare-Earth Elements via Solvent Extraction and the Effects of Diluents. *Journal of Sustainable Metallurgy*. 2017, 3, 601-610.

Paper 4:

Marino Gergoric*, Christian Ekberg, Mark R. St J. Foreman, Britt-Marie Steenari, Teodora Retegan. Characterization and Leaching of Neodymium Magnet Waste and Solvent Extraction of Rare-Earth Elements using TODGA. *Journal of Sustainable Metallurgy*. 2017, 3, 638-645.

Paper 5:

Marino Gergoric*, Christian Ekberg, Teodora Retegan. Mixer-Settler System for the Recovery of Neodymium, Praseodymium and Dysprosium from Organic Acids Leachates of Neodymium Magnets. To be submitted for publication to *Separation and Purification Technology*, 2018.

Contribution report:

Papers 1-2: main author, part of experimental work, majority of data analysis and writing.

Papers 3-5: main author, all experimental work, data analysis and writing.

Publications not included in this thesis

Christian Sögaard*, Johan Funehag, Marino Gergorić, Zareen Abbas. The long-term stability of silica nanoparticle gels in waters of different ionic compositions and pH values. *Colloids and Surfaces*. 2018, 554, 127-136.

Contribution: majority of the measurements

Marino Gergoric*, Christian Ekberg, Britt-Marie Steenari, Teodora Retegan. Organic Phase Optimization in Solvent Extraction of Rare-Earth Elements from Neodymium Magnet Leachates. *ERES 2017 International Conference*, Santorini, Greece. 2017.

Contribution: main author, all experimental work, data analysis and writing.

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1. INTRODUCTION

In a world of growing economies based on research and development, the supply of raw materials is crucial. Since the resources of raw materials are finite and their prices can fluctuate significantly due to political and economic reasons, new methods of recycling raw materials from end-of-life products and appliances are being developed. Furthermore, having linear economies based on the mine-use-dispose principle has taken a huge toll on the environment and is unsustainable in the long run. This is why the move towards circular economies [1] that involve the cyclical flow of materials and energy is currently promoted by the EU and countries across the globe. Recycling of metals and other substances from end-of-life products cannot completely replace the need for mining in growing economies but it can significantly decrease the dependence on raw materials and help stabilize their prices [2]. Large interest is being focused on research investigating recycling of critical elements in the EU, most notably the rare earth elements (REEs) [3-6].

REEs possess great magnetic, spectroscopic and catalytic properties. This has made them some of the most crucial materials in the industry today. They are especially interesting because they play a big role in the transition to a low-carbon economy through products such as high-efficiency magnets, catalysts, electronics used in hybrid vehicles to reduce the consumption of gas [7], wind turbines that produce clean energy, semiconductors etc. Life as we know it today could also be hard to imagine without RREs, since crucial components of our smartphones, tablets, laptops and smartwatches are made of components that contain REEs as building materials [8]. They are vital components in some widely present products, such as neodymium (neodymium-iron-boron or NdFeB) and samarium-cobalt (SmCo) magnets, lamp phosphors for fluorescent lamps, batteries etc. [3]. China is currently dominating the market by providing over 95% [9] of the global supplies of REEs, which makes their availability in the rest of the world highly dependent on the global political situation and Chinese export quotas. This became painfully obvious during the 2011 REEs crisis [3] when prices skyrocketed. Today, in 2018, after prices have stabilized and although a repeat of the REEs crisis that occurred in 2011 is unlikely [10], the EU Commission still lists REEs as the most critical elements according to supply risk [11]. However, recycling rates for REEs in the EU are still at disappointingly low levels, amounting only to around 6-7% [11].

While the use of REEs in lamp phosphors and NiMH batteries is declining [9], the demand for REE-based magnets is expected to grow over the period 2010-2035, with an expected annual growth of 5.3% [5]. NdFeB magnets are the most common permanent magnets on the market, due to their high energy production of 512 kJ/m³ (theoretic maximum) [5]. They have been used in hard disk drives (HDDs), electric cars, electric bikes and large generators of electricity in wind turbines [12], meaning their waste is expected to grow and be available for recycling in the future, although there are still issues with separating the permanent magnets from the rest of the waste and other ferrous parts. The amount of REEs in the NdFeB magnets is usually around 30% (mainly Nd, with small admixtures of Dy, Pr, Gd and Tb) [4], which is higher than in the ores that the REEs are usually mined from [13]. Considering the above, end-of-life NdFeB magnet scrap is a feasible source for the recycling of REEs.

Hydrometallurgical recovery of REEs from NdFeB waste, currently mostly performed on a research level, is an attractive way of recycling since it is efficient and high purity fractions can be achieved. This method is also not as energy intensive as the pyrometallurgical methods [3, 4, 14-17]. The processes usually involve leaching of the waste, extraction of the REEs from the obtained leachate, stripping of the elements of interest into a new aqueous solution, and precipitation or further reprocessing. High amounts of Fe in the NdFeB waste can make this route problematic since the Fe needs to be separated from the REEs. Leaching usually requires large amounts of strong mineral acids to achieve high leaching efficiencies [18, 19]. This can have an adverse impact on the environment in cases of accidental release and poisonous gas release during leaching. In the solvent extraction step, large amounts of phosphorous containing organic compounds that cannot be incinerated are used, thus producing ash, acidic gasses and large amounts of other toxic chemicals [14].

1.1. Scope and motivation

The main objective of the work performed in this thesis was to find feasible ways of selectively separating the REEs from NdFeB waste. To this end, leaching was used to dissolve the NdFeB magnet waste and solvent extraction was used to selectively extract the REEs from the obtained leachates. Throughout this research the leaching and solvent extraction processes were mitigated considering the efficiency of the process and the environmental impact of the process. The highlights of the work can be summarized as:

- (a) Selective recovery of the REEs from other components in the NdFeB magnet waste, such as Fe, Co, B and Ni was obtained.
- (b) Leaching was performed using both inorganic and organic acids. Inorganic acids have been attractive due to their high leaching efficiency and overall cost. Organic acids have been very scarcely investigated in the leaching of NdFeB magnet waste streams and can have advantages over the use of inorganic acids in terms of environmental impact. The parameters that were monitored during the leaching process were leaching kinetics, acid concentration, temperature and solid-to-liquid ratio effects on the leaching.
- (c) Solvent extraction processes were performed and optimized according to critical parameters, including extractant concentration, kinetics, aqueous phase pH and diluent effect on extraction. Extractants such as tetraoctyl diglycolamide (TODGA) that follow the CHON principle [20] and are completely incinerable without carbon residue was used to explore new alternatives to the phosphorous-dominated solvent extraction processes currently being studied in development of new recycling processes and widely used for recovery of REEs from primary ores in China [3].
- (d) A process was developed up to pilot scale based on the use of organic acids leachates in solvent extraction separation of REEs.

2. BACKGROUND

2.1. Rare-earth elements

The elements Sc and Y plus the lanthanides, which are chemically closely related, make up the REEs group [21]. There are two main classifications of REEs. The first divides them into d-block elements (Sc and Y) and the f-block elements or lanthanides (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu). Sc and Y are added to the REEs group due to their chemical similarity and occurrence in nature [22]. The second classification method divides them into light rare earth elements (LREEs, La-Gd) and heavy rare earth elements (HREEs, Tb-Lu and Y). Although Sc is the lightest LREE, it is not classified under the LREEs because its electron configuration is not comparable with the LREEs group. Although their name might suggest that they are very scarce and hard to find in nature, they are actually quite abundant in the earth's crust, however usually not in economically feasible exploitable forms due to dispersion [13]. Furthermore, due to their chemical similarity they occur in mixtures [23] and are very difficult to separate from each other. Since industrial applications of REEs usually require them to be in a chemically pure form, or in a certain concentration together with some other elements, their separation and purification is crucial.

The LREEs are characterized by the increasing number of unpaired electrons from 0-7 and the HREES have an increasing number of paired electrons from 8-14 [21]. In solutions the REEs ions are usually in the 3+ state due to the stability of their f-orbitals, although there are some exceptions like Ce^{4+} , Eu^{2+} and Yb^{2+} . Being hard Lewis acids, the chemical bonding of REEs is usually of ionic character, with limited covalent character. In aqueous solutions they are characterized by small ionic radii, high oxidation states, high electronegativity and low polarizability [24]. An important property of the REEs is known as lanthanide contraction, which suggests the decrease of the ionic radii from La – Lu is much more pronounced in this particular period than others. The ionic radius decreases due to imperfect shielding of the valence f-orbitals. Due to size limitation of the 4f-orbitals the lanthanides' atomic size is defined by 5s and 5p. Since the 4f orbitals' extension is limited they do not overlap with other orbitals, making it very unlikely that they will create covalent bonds with other elements[25].

As already mentioned, REEs are used in a wide variety of products and devices. The applications of each of the 17 REEs are presented in Table 2.1.

Table 2.1. Application of various rare earth elements (REEs) in the industry [4, 26, 27]

Element	Applications
Scandium (Sc)	Sc-strengthened alloys with high performance
Yttrium (Y)	Fluorescent lamps, plasma displays, CRT screens, NiMH batteries
Lanthanum (La)	Fluorescent lamps, NiMH batteries
Cerium (Ce)	Fluorescent lamps,
Praseodymium (Pr)	NdFeB magnets, NiMH batteries
Neodymium (Nd)	NdFeB magnets, NiMH batteries, CRT screens
Promethium (Pm)	Beta source, atomic batteries
Samarium (Sm)	SmCo magnets, CRT screens
Europium (Eu)	Fluorescent lamps, plasma displays, LEDs
Gadolinium (Gd)	Fluorescent lamps, LEDs, NdFeB magnets
Terbium (Tb)	Fluorescent lamps, CRT screens
Dysprosium (Dy)	NdFeB magnets
Holmium (Ho)	Lasers, nuclear applications
Erbium (Er)	Absorbing glass, fiber optics
Thulium (Tm)	X-ray
Ytterbium (Yb)	Pressure sensors, optics
Lutetium (Lu)	Few commercial applications, mostly catalysis and optics

2.2. Neodymium magnets

Neodymium magnets (NdFeB, Nd₂Fe₁₄B or neodymium-iron-boron magnets) are one of the most important applications of REEs since they are the strongest permanent magnets currently available on the market with maximum energy production, expressing the performance of the magnet, reaching 512 kJ/m³ [5]. Due to their excellent magnetic properties they have found numerous technological applications, including HDDs, electric and hybrid vehicles, electric bikes, wind turbines, and small-scale electrical appliances [3-5].

The chemical composition varies significantly, depending on the specific application, but in principle all the NdFeB magnets are composed of a tetragonal Nd₂Fe₁₄B crystalline structure [28]. They are composed of around 30% of Nd, 64% of Fe and 0.5 % of B [19]. The matrix made up of Nd₂Fe₁₄B is surrounded by a Nd-rich grain boundary. Other REEs found in the grain boundary are Dy, Gd, Pr and Tb [3]. Other elements, including Al, Co, Cu, Mo, Nb, Ti, V and Zr, can also be found in small amounts. The addition of certain elements is directly connected to enhancement of certain properties. To this end, small amounts of Dy and Tb are added to increase the intrinsic coercitivity and anisotropy of the magnet and the performance of the magnet at high temperatures. Gadolinium is added to increase the temperature coefficient, while Cu and Al are added to improve sintering of the magnet [5]. Cobalt, on the other hand, is added to increase the Curie temperature of the magnet [29], which is the temperature at which it loses its magnetic properties. Furthermore, Ni-based coatings [30] are used to protect the surface of the NdFeB magnets from corrosion. The typical composition of the NdFeB magnets, according to various sources, is presented in Table 2.2.

Table 2.2. The elemental composition of NdFeB magnets according to various sources [3-5, 14, 18]

Element	Elemental composition / w.t. %			
Nd	25.3	25.95	25	21-31 (Nd+ Pr)
Pr	2.62	0.34		
Dy	1.08	4.21	4	0-10
Fe	61.1	58.16	69	
Co	1.42	4.22		
B	1.00	1	1	
other		1		

Since their introduction in 1983 [31] NdFeB magnets have largely dominated over the SmCo, alnico and ferrite magnets, due to their superior magnetic properties, and this is expected to stay the case in the magnet industry in the years to come [3, 5, 9].

2.3. Recycling of neodymium magnet waste

Appliances and products containing RREs are widely used in almost every industry today [6] and their supply in the last decades has become critical for many areas of human development and is expected to grow in the future. Due to various legislative and economic factors [3, 4], around 95% of the global need for REEs is supplied by China, despite it possessing only 40% of the proven global REE reserves. This makes China a dominating REE market, with new knowledge on REE recovery being developed there, while Europe and other parts of the globe are stagnating in that regard. Although their prices have decreased significantly since the global REE crisis in 2011, they are still considered the most critical elements by supply risk in the EU [11] and new incentives for their recycling are being developed.

Due to their high amount of REEs (Table 2.2.), neodymium magnets are seen as a feasible source of REEs such as Nd, Pr and Dy. Furthermore, according to predictions (Figure 2.1.), neodymium magnets are expected to be the most in-demand materials, mostly due to the development of green energy sources such as wind turbines and electric vehicles for transportation.

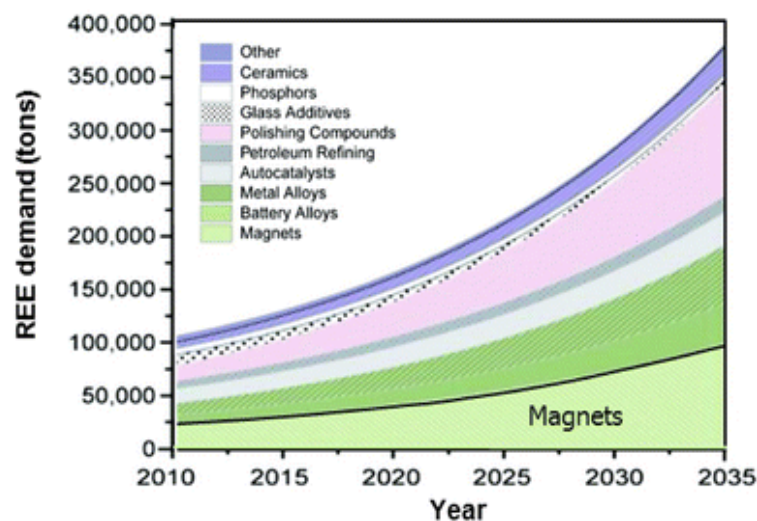


Figure 2.1. Prediction of demand for REEs according to demand (2010-2035) [32].

In a study by Habib et al. [33] (2014) it was predicted that the recycling from secondary sources could, by current trends, meet the demand for 50% of the Nd and Dy by 2100. Reusing neodymium magnets would be the most efficient way, since they largely retain their magnetic properties. This is possible only with large, readily available magnets present in wind turbines or electric vehicles [3], but special care has to be taken concerning their corrosion properties. They are easier to take apart and separate from the source, but these magnets have a long lifespan and will not be readily available for large-scale recycling in the near future. On the other hand, more available sources of neodymium magnets are electrical bikes, HDDs, loudspeakers, smartphones and other consumer electronics [4, 5]. These are usually glued or fixed in another way to other structural parts and their disassembly from other parts is often needed. In the recycling methods used for consumer electronics today, most of the permanent magnets are lost and end up in slag residues from pyrometallurgical and hydrometallurgical recovery processes for more common metals [33]. The incentive for companies to dismantle and shred electronic waste is currently only driven by the market value of the REEs, which is unfortunate since this step is the key step for further efficient metallurgical recovery and further possible legislations will be needed to encourage the recovery of the magnets. Dismantling and separation methods to be used before shredding have been studied and presented at Hitachi corporation in Japan [34], University of Birmingham [12] and some projects such as EREAN (<http://erean.eu>).

Recovery of REEs from neodymium magnets after disassembling, hydrogen decrepitation [12] and shredding can be done by hydrometallurgical and pyrometallurgical methods. Pyrometallurgical methods are usually applicable for all types of magnets, they generate no aqueous waste, fewer steps are usually needed than in a hydrometallurgical process and REEs can be obtained in a metallic state. However, these methods have some disadvantages, including large energy input and solid waste, e.g. slag, production [3]. Hydrometallurgical methods that are commonly used for recovery of REEs from primary ores, on the other hand, are efficient for achieving high purity REEs, but create significant amounts of waste water and involve environmentally problematic chemicals. Efficient recovery of REEs usually involves using both pyro and hydro methods but further development of both recovery routes is needed. This work has focused on improving hydrometallurgical recovery of REEs from neodymium magnets and the present status for those methods will be further discussed in the following section.

2.4. Hydrometallurgical treatment and recovery of REEs from neodymium magnets

Hydrometallurgical methods are a feasible way to recover REEs from REE-rich end-of-life waste. The hydrometallurgical recovery process usually consists of the following steps:

- (a) *leaching* (digestion, dissolution) of the waste stream, usually powder of crushed material, to achieve an REE-rich aqueous phase liquor for further reprocessing [35-39].
- (b) *solvent extraction* or *ion exchange* of the REEs from the REE-rich aqueous liquors, followed by stripping of the extracted species [40-43].
- (c) *precipitation* or *electro deposition* or further reprocessing of the strip solution [44].

An overview of the current state-of-the-art in the field of hydrometallurgical recovery of REEs from neodymium magnets will be presented in the following subchapters.

2.4.1. Leaching

In the NdFeB magnet leaching step, the main goal is to completely transfer the REE elements into the aqueous solution. Co-leaching of Fe and other elements into the solution can pose some challenges in further purification, which is why leaching selectivity is the aim. Selective extraction of Fe is only a part of the solution, since other components including B, Co and Ni can also be present in noticeable quantities [14].

Mineral acids such as HCl, HNO₃ and H₂SO₄ are commonly used in the leaching of end-of-life NdFeB waste. The current achievements in the NdFeB waste leaching field are listed in Table 2.3.

Table 2.3. Optimal conditions for leaching of REEs NdFeB magnet waste using some common inorganic acids, as reported in the literature.

Leaching agents	Optimal acid concentration	Solid-to-liquid ratio	Optimal temperature	Leaching time	Reference
H ₂ SO ₄	2 mol/L	1/10 kg/L	-	24 hours	[15]
H ₂ SO ₄	3 mol/L	110.8 g/L	70 °C	4 hours	[45]
H ₂ SO ₄ , HCl, HNO ₃ and NaOH	3 mol/L HCl and 1.5 mol/L H ₂ SO ₄	20 g/L	27 °C	15 minutes	[46]
HCl	0.5 M HCl	100 g/L	368 K	300 min	[47]

Since these acids also leach high amounts of Fe from the waste, special attention has been focused on developing some REE-selective processes, like the one developed in 2016 by Önal et al.,[48], where a selective leaching process for REEs, leaching Fe in the solid residue was developed. The NdFeB magnet powder sample was turned into a sulfate mixture by mixing with concentrated H₂SO₄ (12 – 16 mol/L) in crucibles. After drying and high-temperature treatment, the powder was leached in demineralized water for 15 min to 24 h, which led to >95% recovery of REEs, while Fe remained in the solid residue in the form of a sulfate. In conclusion, most of the research so far has been conducted using strong mineral acids for leaching [14, 49-51].

Leaching of REEs out of NdFeB magnets using mineral acids such as HCl, HNO₃ and H₂SO₄ is very efficient. However, utilization of strong mineral acids can cause some adverse impacts on the environment [19, 52, 53] due to issues with the regeneration of the acids used and handling, which can be challenging in some situations. In the case of accidental release of highly concentrated acids to the environment, this could acidify the soil, which would require further soil neutralization treatment [54]. Moreover, when leaching is performed using strong mineral acids, evolution of poisonous gases is often a problem. HCl (a non-oxidizing acid) dissolves most non-noble metals, accompanied by evolution of flammable hydrogen gas.

HNO_3 reacts with most metals except Au and Pt, with the release of either H_2 or NO_x depending on concentration and metal. H_2SO_4 (diluted) reacts with metals such as other mineral acids, liberating hydrogen gas, while H_2SO_4 (concentrated) can also dissolve some noble metals such as Cu, Ag, and Hg, accompanied by evolution of SO_2 . These types of gas producing reactions are specifically coupled to the leaching of metallic wastes and do not occur when leaching waste containing already oxidized metal species. Thus, further research is needed in order to minimize the environmental impact of leaching of metallic wastes on the environment. Using organic acids [55] could have advantages in this regard because of easier handling, less poisonous gas evolution due to lower acidities, and much easier degradability. Organic acids have been used before in f-block elements separations [21, 56] and could be appropriate for reclaiming REEs out of NdFeB magnet waste since they form soluble complexes with REEs. As citric and acetic acids are in high demand both in the chemical and food industry, the price is comparable to that of mineral acids. They can also be quite cheap, thanks to some industrial processes using microbiological fermentation [57], and are less harmful to dispose of than highly concentrated inorganic acids.

The leaching of neodymium magnets using organic acids has been very scarcely investigated. The kinetics of extraction of Nd out of NdFeB waste using acetic acid was investigated in detail by Behera et al. [19] in 2016. The study showed that acetic acid in concentrations higher than 0.4 mol/L at 800 rpm, 1% (*w/v*) and 308 K was effective at leaching Nd and Fe out of the waste. However, in this study—as well as in other works—little attention was paid to the recovery of other REEs, meaning no detailed study of the kinetics or temperature-dependence was performed for vital REEs such as Dy and Pr in the waste. The behavior of other impurities such as Fe, B and Co during the leaching process was not completely addressed either. Furthermore, the feasibility of solvent extraction of REEs from the acetic acid based leachates was also not sufficiently studied.

2.4.2. Solvent extraction

There are a wide range of extractants that have previously been used for selective extraction of REE ions out of REE-rich leachates, some on a large-scale and some only on a small-scale, tied to basic research. Some of these are acidic extracts, such as D2EHPA (di-(2-ethylhexyl)-phosphoric acid) [17, 58], PC88A (2-ethylexyl hydrogen 2-ethylhexyl phosphonate, HEHEHP) and Cyanex 272 (di-(2,4,4-trimethylpentil) phosphinic acid), while solvating extractants such as Cyanex 923 (mixture of trialkyl-phosphine oxides) and TODGA (tetraoctyl-diglycolamide) have also been successfully employed [44, 59]. The scientific background of solvent extraction is presented in the Theory chapter (pages 10-17).

In order to achieve good separation of the REEs it is necessary to choose a proper, and as selective as possible, complexing agent [60]. In the separation of the REEs organophosphorous extractants are commonly used [16, 61, 62]. As already mentioned, di(2-ethylhexyl)-phosphoric acid (D2EHPA), an acidic extractant, is commonly used on a larger industrial scale [63]. The selectivity order for extracting rare earths from 0.5 M HCl solution with 0.75 M D2EHPA in toluene was found by Peppard and coworkers to be $\text{Lu} > \text{Yb} > \text{Tm} > \text{Tb} > \text{Eu} > \text{Pm} > \text{Pr} > \text{Ce} > \text{La}$, with the log of the distribution coefficient increasing linearly with the atomic number of the rare earth element [64]. D2EHPA has also been used to separate Sm, Eu, and Gd from the other rare earths in a mixed nitrate-chloride leachate from monazite, with general

formula $(\text{Ce},\text{La})\text{PO}_4$ [65]. Furthermore, in many studies [66] it was shown that a typical separation factor between adjacent REEs using the D2EHPA extractant is in the region of 2.5. Separation of neodymium and dysprosium ions in solution has been achieved with organophosphorous extractants such as PC-88A by Tanaka and coworkers [6]. A separation factor of 525 was obtained at pH 1.1. Scrubbing of the neodymium ions that are extracted alongside dysprosium ions is done with dysprosium chloride or dilute hydrochloric acid solutions [4]. The developed processes nowadays are still mostly tied to basic research and are seldom used on an industrial scale for recycling of REEs out of leachates obtained by dissolving E-waste [4, 5, 14, 17, 50].

The extracting agents mentioned, although cheap and readily accessible, have some disadvantages, such as poor selectivity between REEs and other exogenes, poor stripping of the metals from the organic phase and a low rate of extraction. Moreover, few of the rare earth extraction agents currently used in industry follow the CHON principle, meaning it is not possible to incinerate them without either the production of ash or acidic gases [20]. A promising extractant that complies with the CHNO principle and could be used for the extraction of REEs out of the leachate formed from NdFeB magnet waste is TODGA (N, N, N', N'-tetraoctyl-diglycolamide). This molecule has previously shown good extraction properties of lanthanides and actinides when extracted from highly acidic solutions [67, 68]. It has also been found that the loading capacity of 0.1 M TODGA-n-dodecane is 0.008 M Nd(III) with an aqueous phase of 3 M HNO_3 [67]. An especially interesting fact for this research is that very low distribution ratios ($< 10^{-2}$) of Fe (III) and Al(III) were observed during extractions with 0.1 TODGA in n-dodecane from 2.9 M nitric acid, since aluminum and iron are expected to be present in the leachate produced in the leaching of neodymium-based magnet material [68].

In recent years new ionic liquids have been developed as a replacement for organic extractants. [29] These are a more environmentally friendly alternative to traditional solvent extraction using organic solvents but are scarcely used today, even in research, while their large-scale use is far from being feasible due to problems with solubilization losses and viscosity. [69]

Large-scale hydrometallurgical treatment of NdFeB waste has only really taken off in the last few years. This is because recycling of NdFeB could not be justified from an economical point of view, only from an environmental one, unlike the recovery of Sm and Co from the SmCo magnets [3]. There are therefore very few developed large-scale NdFeB hydrometallurgical recovery routes.

In 2015, at the Oak Ridge National Laboratory, Tennessee, a process utilizing membrane solvent extraction was conducted that compared the extraction of REEs from a neodymium magnet leachate with traditional solvent extraction using Cyanex 923 and TODGA. With TODGA Nd, Dy and Pr were selectively recovered with no co-extraction of non-REEs such as Fe and B [70]. Another process for separating REEs (Nd, Dy, Pr and Tb) from a neodymium magnets waste stream was developed using PC-88A on a pilot scale mixer-settle battery by Elwert et al. [71] in 2017, with promising results. Twelve stages were needed for achieving high purity 4N (99.99%).

3. THEORY

3.1. Leaching

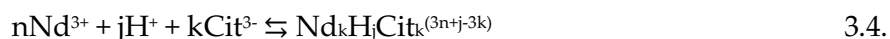
Leaching is the process of extraction of certain elements or compounds from a solid and dissolving it into a liquid. This is commonly done e.g., in the industrial recovery of metals from ores, but is also used in the recovery of valuable elements such as REEs from electronic waste. Inorganic acids, including HNO_3 ($\text{pK}_a = -1.4$), HCl ($\text{pK}_a = -5.9$), and H_2SO_4 ($\text{pK}_{a1} = -3$, $\text{pK}_{a2} = 1.99$) are commonly used. The following equations illustrate how the acids, represented as dissociated hydrogen cations, leach the rare-earth elements, regardless of their potential oxidized form: [72]



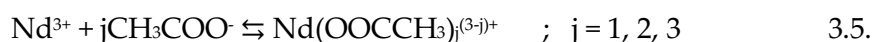
Parameters including leaching kinetics, solid to liquid ratio, leaching temperature and stirring speed are monitored and modified in order to increase the leaching efficiency and decrease the cost of the overall leaching process.

Organic acids, although weaker (higher pK_a) than the inorganic acids, can also be used for leaching of electronic waste. Organic acids used in this work were citric, acetic, glycolic, maleic and ascorbic acid. They were used due to their availability and price, which is comparable to those of inorganic acids. Using these acids could have environmental benefits compared to inorganic acids, as discussed in the Background section.

Citric acid (Figure 3.1. a)) contains three carboxylic groups, with the three hydrogen dissociation constants being $\text{pK}_{a1} = 3.13$, $\text{pK}_{a2} = 4.76$, $\text{pK}_{a3} = 6.40$ at 25°C and zero ionic strength [73]. Two possible mechanisms of dissolution with citric acid include metal ion displacement with hydronium ions, and formation of soluble metal ion-ligand complexes by metal ion chelation. [74] A study by Brown et al., [75] reported that the Nd^{3+} complex with the citrate counter-ion is formed according to the following equilibrium (Equation 3.4.):



The existence of NdCit , NdHCit , NdHCit_2 and NdCit_2 was confirmed in the solution in the pH range 2-5 using XAFS (x-ray absorption fine structure), which proves citric acid could be used for the leaching of Nd and other REEs out of E-scrap. *Acetic acid* (Figure 3.1. b)) is an organic acid containing one carboxylic group with $\text{pK}_a = 4.76$. Work by Zanonato et al., [76] reported that Nd^{3+} forms at least three successive mononuclear complexes according to the following equilibrium (Equilibrium 3.5.):



This indicates that acetic acid could be used for leaching of Nd and possibly other REEs from electronic waste. *Maleic acid* is a strong diacid. Since it is a cis-isomer (Figure 3.1. c)) it is capable

of forming intra-hydrogen bonds, which makes the conjugated base much more stable than its trans-isomer, fumaric acid. *Glycolic acid* is stronger than acetic acid due to the electron withdrawing power of the hydroxyl group (Figure 3.1. d)) [77]. *Ascorbic acid* is much more acidic than would be expected thanks to its double bond, which allows stabilization by delocalization of electrons (Figure 3.1. e)). Regarding their acidities, glycolic, maleic and ascorbic acid can be ranked according to their first acidity pK_{a1} : maleic (1.9) < glycolic (3.8) < ascorbic (4.1) (meaning that maleic acid is the strongest of the three). Furthermore, both maleic and ascorbic acids are di-acids (pK_{a2} being 6.1 and 11.7, respectively). The following equations illustrate the behavior of glycolate and maleate anions in solution, respectively, and their interactions with metallic cation such as REE cations.

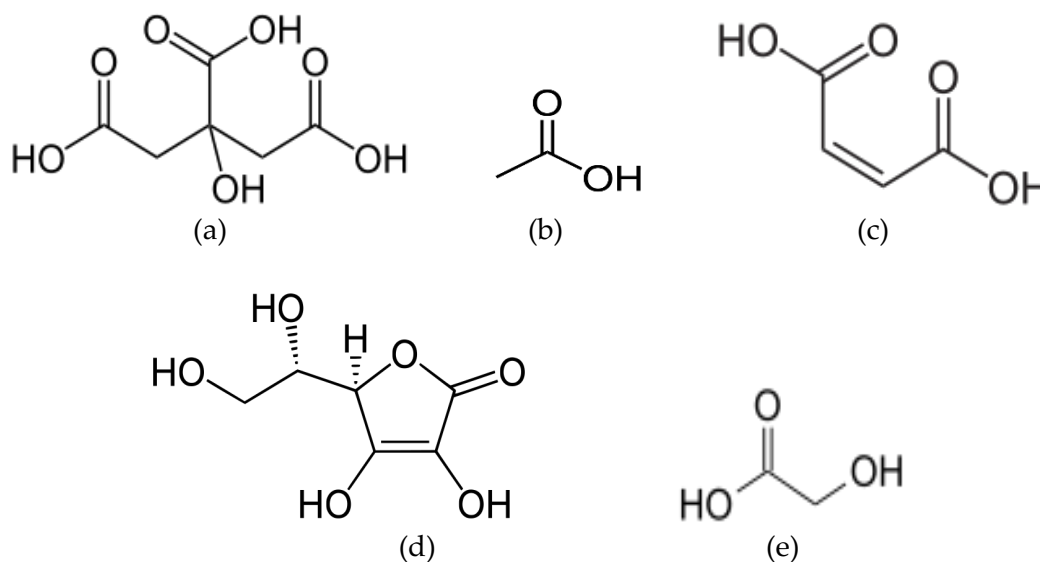


Figure 3.1. Structural formulas of (a) citric acid, (b) acetic acid, (c) maleic acid, (d) glycolic acid and e) ascorbic acid.

3.2. Solvent extraction

Solvent extraction, also referred to as liquid-liquid extraction, is a process of transfer of a dissolved substance (solute) from one liquid phase to another liquid phase. The liquid phases should be immiscible or partially miscible. [78] Most commonly these two phases are one aqueous and one organic phase. The aqueous phase is rich in the solute to be extracted, most commonly metal ions, while the organic phase is the solvent into which the solute is to be extracted. The solvent in the organic phase is made up of the extracting agent dissolved in a diluent, with possible addition of a modifier to prevent the formation of a third phase.

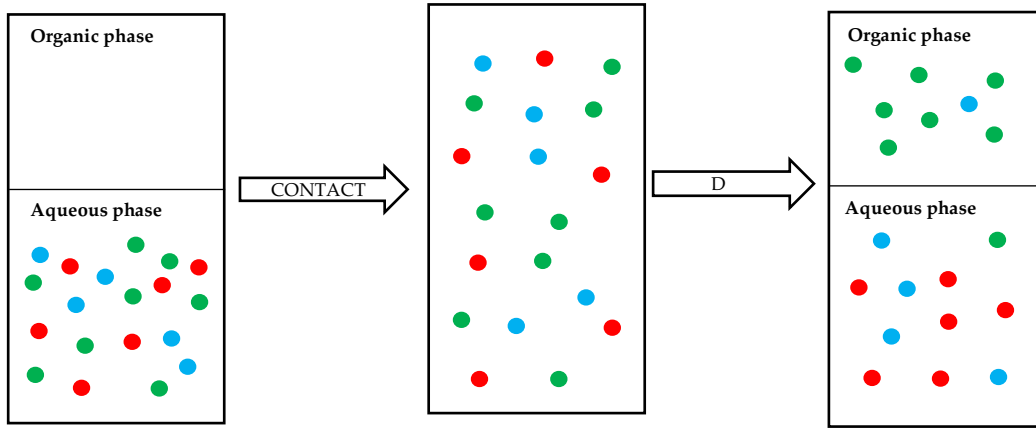


Figure 3.2. Schematics of a solvent extraction process. (a) Organic phase and aqueous phases before contact. (b) The two phases are brought into contact by shaking or stirring. (c) After contact, the two phases are separated and the solute is distributed between the phases depending on the chemistry of the system.

Solvent extraction has a wide range of applications, including nuclear reprocessing, metal recovery from aqueous solutions and production of organic compounds. [24] Some factors that need to be considered when choosing an appropriate extracting agent [79, 80] are the cost, immiscibility with the aqueous phase, chemical stability, solubility in organic diluents, chemical selectivity for the solute of interest and its environmental safety characteristics.

The efficiency of the extraction steps is described by determining the distribution ratio (D), which is the most important parameter, and the separation factors (α). These are calculated using the following equations:

$$D_A = \frac{[A]_{org}}{[A]_{aq}} \quad 3.8.$$

$$\alpha_{A/B} = \frac{D_A}{D_B}; \quad D_A > D_B \quad 3.9.$$

Where $[A]_{org}$ and $[A]_{aq}$ are the equilibrium concentrations of the metal of interest (A) in all its existing species in the organic and aqueous phase, respectively. In this work, the concentration in each phase was calculated as a mass balance of the solute in the aqueous phase before and after extraction, which can have some limitations. The separation factor represents the selectivity between two metals in the extraction. The ratio between the organic and aqueous phase is defined by Equation 3.10.

$$\theta = \frac{V_{org}}{V_{aq}} \quad 3.10.$$

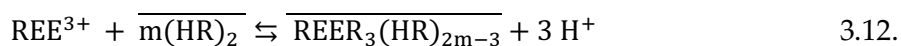
The fraction extracted, or recovery factor [78] is defined as:

$$E = \frac{\theta D_A}{1 + \theta D_A} * 100 \% \quad 3.11.$$

3.2.1. Extracting agents in solvent extraction

For the transport of the element from the aqueous to the organic phase, the ionic species in the aqueous phase need to be chemically modified to be soluble in the organic phase. The organic molecular species involved in this process are called extractants (extracting agents) and, depending on the mechanism of the extraction of the metal ion from the aqueous phase into the organic phase, they can be classified in three main groups: [80]

ACIDIC: the organic acid dissociates and its conjugated base reacts with the cation to form a neutral complex according to Equation 3.12: [16]



$$D_A = \frac{[\overline{\text{REER}_3(\text{HR})_{2m-3}}]}{[\text{REE}^{3+}]} \quad 3.13.$$

where HR represents the associated acidic extractant molecules and REE the rare-earth ion in the solution. Common acidic extractants used are D2EHPA (Figure 3.3. (a)), Cyanex 272 (Figure 3.3. (b)), HEHEHP etc.

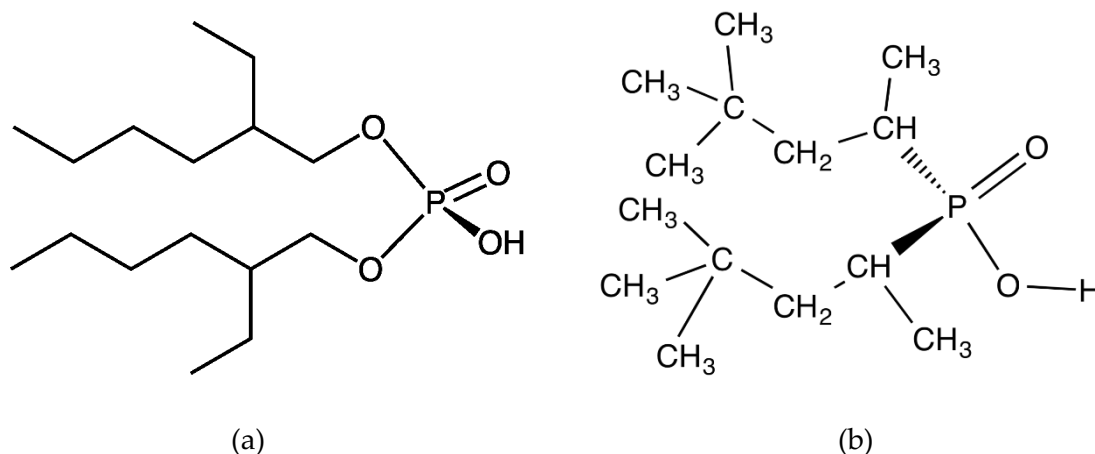
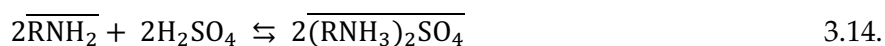


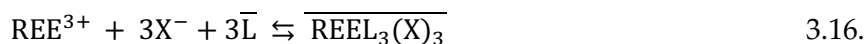
Figure 3.3. Structural formulas of (a) D2EHPA and (b) Cyanex 272

BASIC/ION PAIR: the organic species forms an ion pair with the negatively charged metal complex in the aqueous phase according to Equations 3.14 and 3.15.:



where RNH_2 represents the tri-alkyl methylamine and REE represents the rare-earth ion in the aqueous solution. This extraction mechanism is only possible in the presence of strong anionic ligands.

SOLVATING: the hydrating water in the inner sphere of the metal atom is replaced with the organic species according to Equation 3.16:



$$D_A = \frac{[\overline{\text{REEL}_3(\text{X})_3}]}{[\text{REE}^{3+}]} \quad 3.17.$$

L represents the ligand molecule and REE the rare-earth ion in the aqueous solution. Commonly used solvating extractants are TODGA (Figure 3.4. (a)), TBP (Figure 3.4. (b)), Cyanex 923 etc.

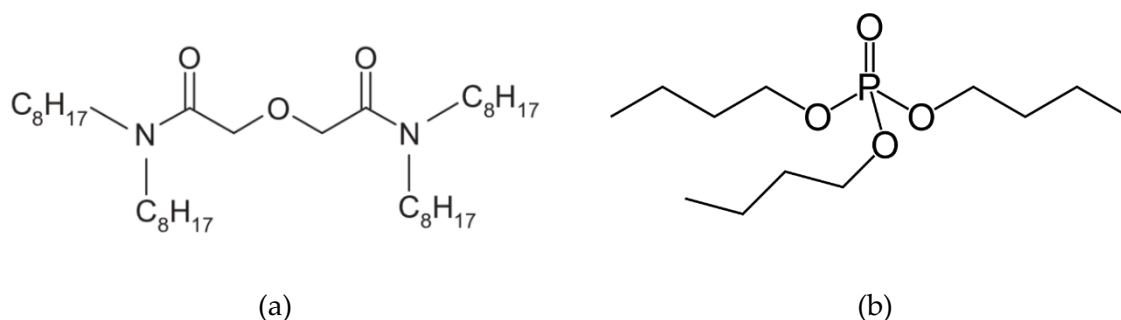


Figure 3.4. Structural formulas of (a) TODGA and (b) TBP.

3.2.2. Diluents in solvent extraction

A diluent is a liquid or homogenous mixture of liquids in which extracting agent(s) and modifier(s) are dissolved to form the solvent phase. [81] The diluent itself does not extract the solute significantly.

Classifying diluents can be challenging since there are a lot of parameters that have to be considered during their classification, such as solubility parameters, connectivity, dielectric constant etc. No definitive way has yet been found, since each has its disadvantages and drawbacks over the others. [82] According to their chemical and physical properties, such as the ability to form ordered networks, diluents can be divided into the following groups [24]:

- (a) Liquids capable of forming three-dimensional networks of strong hydrogen bonds, e.g., water, hydroxy acids, polyols and others.
- (b) Liquids containing both active hydrogen atoms and donor atoms (O, N, F) that do not form three-dimensional networks, but instead form chainlike oligomers, e.g., primary alcohols, carboxylic acids, primary amines and others.
- (c) Liquids containing donor atoms but no active hydrogen atoms, e.g., ketones, ethers, aldehydes and others.

(d) Liquids containing active hydrogen atoms but no donor atoms, e.g., chloroform and some other aliphatic halides.

(e) Liquids with no active hydrogen atoms and no donor atoms, e.g., hydrocarbons, carbon disulfide, carbon tetrachloride and others.

The diverse properties of the diluents in a solvent extraction system lead to differences in distribution ratios of the solute and the overall extraction process. The group (c) diluents often have the ability to extract the solute without further addition of an extractant. The group (d) and (e) liquids do not dissolve salt without the addition of the extractant and are often used as diluents in a solvent extraction system. Group (b) primary alcohol diluents have the ability to form hydrogen bonds. They have both active hydrogen atoms and donor atoms for hydrogen bond forming, which can affect the solubility of the extractant in the diluent negatively and thus lead to lower distribution ratios. The group (a) liquids are easily soluble in water and are impractical from a solvent extraction point of view [24]. Water belongs to this group and it is usually used as a second phase. The polarity of the diluent can also significantly affect the extraction process since the solubility of a neutral complex in an organic phase is inversely proportional to the polarity of the organic diluent. [83] The polarity of the diluent can be characterized by the dielectric constant, also called the relative static permittivity (ϵ), which is a measure of chemical polarity. The values of dielectric constants for the diluents used in this work are shown in Table 3.1.

Table 3.1. The values of the dielectric constant for solvent 70, hexane, octane, cyclohexanone, 1-octanol, chloroform and toluene [84].

Diluent	Dielectric constant (ϵ)
Solvent 70	1.8
pentane	1.84
hexane	1.88
octane	2
dodecane	2.03
cyclohexanone	18.3
1-octanol	10.3
chloroform	4.81
toluene	2.38

Water solubility is an important parameter for the organic diluents since it will affect the phase ratio change and, as stated previously, the organic solvent should be as water-immiscible as possible. The water solubility of the diluents used in this work, expressed as S/mass % at 25 °C, are as follows: solvent 70 (traces), hexane (0.0011), octane(0.000071), cyclohexanone(8.8), 1-octanol (0.054), toluene (0.0531) and chloroform (0.80) [85].

Since the diluents constitute a crucial part of the solvent extraction process, various demands have been formulated as quality measures for diluents. These include low viscosity and low water solubility, a minimal formation of a third phase during the extraction process, as well as a minimal chemical transformation of the diluent in contact with water or other aqueous

phase containments. [86] In cases where the extraction plant is situated in extreme weather conditions the diluents should have high flashpoints and boiling points, as well as a low freezing point.

3.2.3. McCabe-Thiele method

In the upscaling of the solvent extraction lab-scale process into a counter-current bench scale mixer-settler process the number of stages is a crucial parameter to determine. To this end, McCabe-Thiele modelling is a useful method. It consists of plotting a diagram similar to the one shown in Figure 3.5.

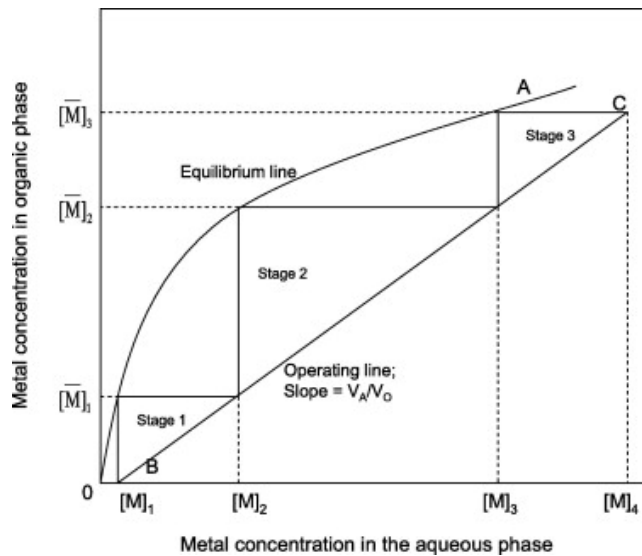


Figure 3.5. McCabe-Thiele diagram for a general counter-current solvent extraction process [16].

The McCabe-Thiele diagram consists of an operating line, an extraction isotherm and the cascade steps. For constructing an operating line, the point representing the concentration of the solute in the aqueous feed (usually rich with the element of interest) and the desired solute concentration in the extract (loaded organic phase) is plotted on the graph, (point C ($[M]_4, [\bar{M}]_3$) in this case). The operating line is then constructed by drawing a line from that point with a slope $1/\theta$ until it intersects the x-axis ($[M]_1$). The isotherm is then constructed by bringing the organic feed and aqueous phase into contact at various θ (for example from 6:1 to 1:6) until the extraction equilibrium is reached. The concentrations of the solute are then determined for each θ and plotted on the graph as solute concentration in the aqueous phases vs. solute concentration in the organic phase. A curve is then fitted through the plotted points that represents the extraction isotherm (in Figure 3.5. this is called the equilibrium line). If the θ stays the same throughout the extraction process and the equilibrium is reached in every stage, the ideal number of stages can be determined in the following way:

(a) A horizontal line, parallel with the x-axis, is drawn from point C on the operating line to point A (intersection with the extraction isotherm).

(b) A vertical line, parallel with the y-axis, is drawn from point A to the intersection with the operating line.

(c) Steps (a) and (b) are then repeated in a cascade way until the desired concentration of the solute in the raffinate is reached (preferably as low as possible).

The number of the cascade steps, as shown in Figure 3.5., represent the number of ideal extraction stages.

4. EXPERIMENTAL

The work described in this thesis was focused on the recovery of REEs from neodymium magnet waste using hydrometallurgical methods such as leaching and solvent extraction, as presented in the experimental flow summarized in Table 4.1.

Table 4.1. Experimental outline of the thesis flow.

Experimental section	Experimental steps
(1) Characterization and pre-treatment of the waste	<ul style="list-style-type: none"> • <i>aqua regia</i> dissolution and analysis using ICP-OES/MS. • SEM/EDX and XRD characterization.
(2) Leaching of the waste using different acids	<ul style="list-style-type: none"> • Leaching of waste using acidic lixiviants such as HNO₃, HCl, H₂SO₄, acetic acid, citric acid, glycolic acid, maleic acid and ascorbic acid. • Monitoring and mitigation of variation of parameters such as acid concentration, leaching time, S/L ratio, pH, temperature and stirring speed.
(3) Solvent extraction of REEs using organic solvents	<ul style="list-style-type: none"> • Solvent extraction on the produced leachates using organic extracting agents such as D2EHPA, Cyanex 923, Cyanex 272, TBP and TODGA. • Monitoring of the effects of parameters such as extracting agent concentration, extraction kinetics, aqueous phase pH and counter-ion concentration. • Monitoring of the effect of the following diluents on extraction: Solvent 70, pentane, hexane, dodecane, octane, 1-octanol, cyclohexanone and toluene.
(4) Laboratory pilot-scale separation of REEs	<ul style="list-style-type: none"> • Development of a pilot-scale process for the recovery of REEs from organic acids leachates using mixer-settler batteries.

All the experimental sections and steps listed in Table 4.1 will be discussed in the following subsections.

4.1. Characterization and pre-treatment of the waste

Hydrogen decrepitated (HD) NdFeB magnet powder [87] was used as the NdFeB waste stream in this thesis in both original (as received, particle size < 1 mm) and pre-treated forms. Pre-treating was done by roasting at 400 °C for 1.5 hours in an Entech muffle furnace (LF2) in a ceramic crucible. After roasting, the powder was sieved to a particle size of < 355 µm (removing the large coating chunks) using a Retsch AS 200 vibratory sieve shaker. Throughout this thesis,

these two forms of powder will be referred to as HD NdFeB powder and roasted NdFeB powder, as shown in Figure 4.1. The bright specks in Figure 4.1 (a) represent the magnet-coating residues that are substantially removed after roasting and sieving, as seen in Figure 4.1 (b).

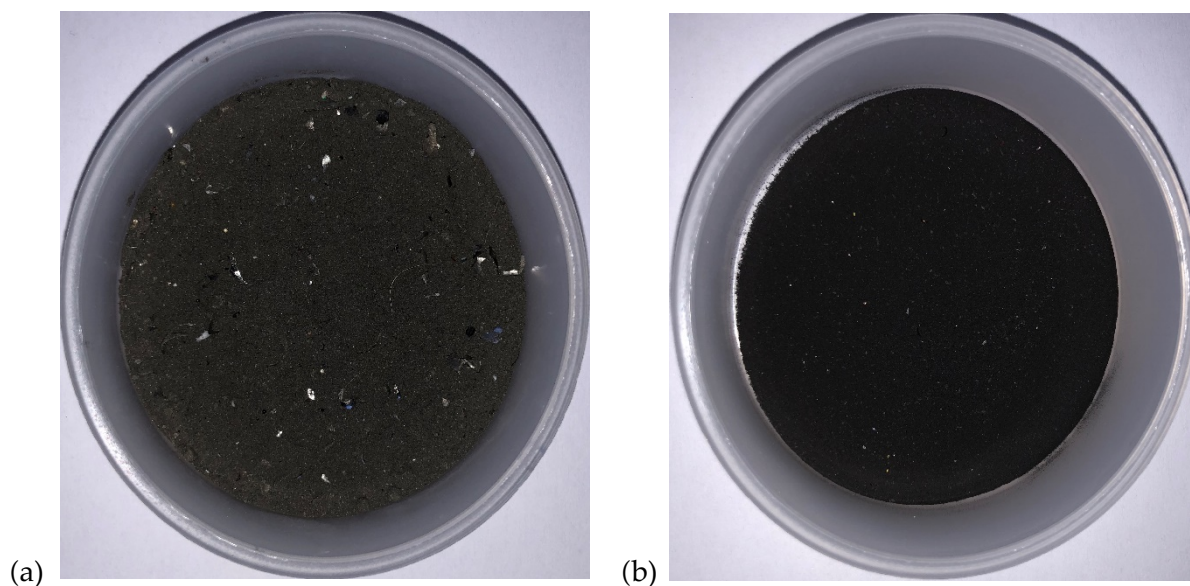


Figure 4.1. Images of (a) HD NdFeB powder and (b) roasted NdFeB powder.

In order to determine the total elemental composition, 1 g of the HD NdFeB powder was dissolved in 10 mL aqua regia (V(conc. HCl):V(conc. HNO₃) = 3:1) at $80 \pm 1^\circ \text{C}$ for 6 hours and was then filtered through polypropylene filters (0.45 μm VWR), while 0.5 g of the roasted NdFeB powder was dissolved in 25 mL aqua regia at $23 \pm 1^\circ \text{C}$ for 6 hours and filtered through Whatman microfiber filters (GF/A 125 and 65 mm diameter). After filtration, the solutions were diluted using 0.5 mol/L HNO₃ (suprapur[®] 65%, Merck). No residues were observed on the filter paper after filtration of either of the solutions. The composition of the prepared solution was measured using ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy, Thermo Scientific iCAP 600 Series ICP Spectrometer) and recalculated into weight percentages of the elements in the powders. All experiments were done in triplicate to ensure statistical reliability of the results. SEM/EDX (Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy) analysis was carried out on the HD NdFeB before and after roasting using a Phenom ProX scanning electron microscope with Phenom ProSuite software and Element Identification module in order to determine whether any surface modifications might have occurred during roasting or if there was any elemental redistribution in the particles. The chemical composition of both the HD and roasted NdFeB powders were further ascertained using x-ray diffraction (XRD Bruker D8 Advance), with Cu K α radiation used to examine the phase content. The 2θ range was $20\text{--}80^\circ$ and step size $0.04^\circ/\text{sec}$. Identification of crystalline compounds was made by comparison with standard data in the JCPDS database.

4.2. Leaching out the REEs from the waste

After the chemical composition of the waste was determined, the leaching experiments were performed using acids of various concentrations and origin. The acids tested were HCl, HNO₃, H₂SO₄, acetic acid, citric acid, glycolic acid, maleic acid and ascorbic acid. The work was divided into leaching using inorganic or organic acids.

4.2.1. Leaching using inorganic acids

Inorganic acids HNO₃ (puriss. p.a., ACS reagent, ≥69%, Sigma Aldrich), HCl (ACS reagent, 37%, Sigma Aldrich), H₂SO₄ (ACS reagent, 95.0-98.0%, Sigma Aldrich) and methanesulfonic acid CH₃SO₃H (Msynth®plus, Sigma-Aldrich) were used as leaching agents. All the acids were diluted to molar concentrations of 1, 2 and 3 mol/L. HD NdFeB powder was used for leaching in inorganic acids at S/L ratio 1/50 g, with a rotation speed of 400 rpm. The leaching system was sampled after 1, 3, 6 and 24 hours, after which the collected samples were diluted in 1 mol/L HNO₃ (suprapur® 65%, Merck) and analyzed using ICP-OES. Leaching efficiency was calculated by comparing the concentration of the elements in the solution to their content in the leached material, determined in the characterization step. The rest of the leachate and the leaching residues (magnet remains) were filtered using a Büchner funnel and Büchner flask. The residues were then completely dissolved in 10 mL of *aqua regia* for 30 minutes ($m_{\text{residue}}(\text{HNO}_3) = 0.27 \text{ g}$, $m_{\text{residue}}(\text{H}_2\text{SO}_4) = 0.03 \text{ g}$, $m_{\text{residue}}(\text{HCl}) = 0.30 \text{ g}$) in glass beakers. The residues dissolution samples were diluted and analyzed using ICP-OES.

4.2.2. Leaching using organic acids

Organic acids acetic acid (Sigma Aldrich, ≥ 99.5%), citric acid (Sigma-Aldrich, ≥ 99.5%), glycolic acid (Sigma Aldrich, >99.5%), maleic acid (Sigma Aldrich, >99.5%) and L-ascorbic acid (Sigma Aldrich, >99.5%) were used as leaching agents for both the HD NdFeB powder and roasted NdFeB powder, prepared by diluting or dissolving the purchased acids with MiliQ water (Merck Millipore Q-POD) to 0.1, 0.2, 0.4, 0.8 and 1 mol/L concentrations. Each sample was reacting in a closed PP plastic cup. For the kinetics study the samples were leached for 100, 200, 300, 400 minutes and 24 hours. Solid-to-liquid ratio was kept at 1/50 g/mL of acid, the temperature at $23 \pm 1^\circ\text{C}$ and stirring speed at 400 rpm on the IKA® RT15 heating and stirring plate. Additional parameters, such as solid-to-liquid ratio, temperature and stirring speed were monitored and mitigated. Solid/liquid ratio was then varied from 1/30 to 1/80 g/mL, using 1 M of all the acids. Furthermore, temperature was varied between $25 \pm 1^\circ\text{C}$ and $70 \pm 1^\circ\text{C}$. Finally, rotation speed was varied between 400 and 1000 rpm. Each experiment was done in triplicate. Powder was weighed on a Fisher MH-214 Analytical scale before the reaction and this was used in the leaching efficiency calculation. The sampled leachates were diluted in 1 mol/L HNO₃ (suprapur® 65%, Merck) and the metal concentrations were measured using ICP-OES. The pH values of the acids before leaching and leachates after 24 h leaching time were measured using MeterLab™ PHM 240 pH/ion Meter pH electrode calibrated using Radiometer Analytical® pH buffers at pH of 4.00, 7.00 and 10.00 (± 0.02 in the temperature interval of 0-25 °C). The reported pH values are the measured proton activities at the specific ionic strength of each solution. The same calibration method was used in all other pH measurements.

More experimental details can be found in [18] and Paper II.

4.3. Solvent extraction of REEs from neodymium magnet leachates

After the optimal leaching conditions were determined, solvent extraction was performed using the obtained leachates and specially prepared organic solvents. Additionally, solvent extraction was performed on a leachate obtained by sulfonation, selective roasting and water leaching [48]. The solvent extraction experiments were divided into the following 3 subsections:

- (a) Extraction of REEs from HNO_3 leachate using TODGA in various diluents [14].
- (b) Extraction of REEs from the leachate obtained by sulfonation, selective roasting and water leaching using D2EHPA in various diluents [17].
- (c) Extraction of REEs from organic acids leachates using D2EHPA, TODGA, Cyanex 923, Cyanex 272 and TBP in various diluents.

a) Extraction of REEs from HNO_3 leachate using TODGA in various diluents

The leachate obtained by leaching HD NdFeB powder with 4 M HNO_3 (S/L ratio 1/50 g/mL, 24 h leaching at 25 ± 1 °C) was used in solvent extraction with TODGA. The aqueous phase for the extraction was prepared by diluting the obtained leachate with 3 mol/L HNO_3 to achieve 4000 mgL⁻¹ of the totally dissolved powder in the solution. The NO_3^- concentration needed was previously determined using an artificial solution containing 21.49 mmol/L Fe, 3.46 mmol/L Nd and 0.62 mmol/L Dy at various HNO_3 concentration and 0.1 mol/L TODGA in Solvent 70. The concentration of HNO_3 after dilution was determined by titration with NaOH (0.1 mol/L NaOH, FIXANAL). TODGA was diluted to 0.01, 0.05, 0.1, 0.2, and 0.4 mol/L using Solvent 70 (hydrocarbons C11–C14, \leq aromatics, Statoil, Sweden), hexane (95%, anhydrous, Sigma Aldrich), toluene (99.8%, anhydrous, Sigma Aldrich), cyclohexanone (\geq 99%, ACS reagent, Sigma Aldrich), and 1-octanol (\geq 99%, ACS reagent, Sigma Aldrich) to test the effect of various diluents on extraction. All the organic phases were pre-equilibrated with an equal amount of 3.1 mol/L HNO_3 .

The solvent extraction experiments were performed in 3.5 mL glass vials shaken using a shaking machine with an adjacent thermostatic bath at 1750 vibrations per minute. Shaking time was 50 min to ensure equilibrium, temperature was 25 ± 1 °C and $\Theta = 1$. Before sampling, the vials were centrifuged at a rotation speed of 2000 rpm for 1 min. The sampled aqueous solutions were diluted with 0.5 mol/L HNO_3 and analyzed using ICP-OES. The distribution ratios were calculated as mass balance using the concentration of the elements in the aqueous solution before and after the extraction. All experiments were done in triplicate.

Stripping was performed using 0.01, 0.1 mol/L HNO_3 (70%, ACS reagent, Sigma Aldrich), and MQ water at $\Theta = 1$ (5 mL/5 mL) for 20 min in 20 mL, shaking the vials at a temperature of 25 ± 1 °C. All the stripping experiments were done in triplicate. The sampled aqueous phases were diluted with 0.5 mol/L HNO_3 and measured using ICP-OES.

More experimental details can be found in [14].

b) Extraction of REEs from the leachate obtained by sulfonation, selective roasting and water leaching using D2EHPA in various diluents

The neodymium magnet leachate was produced through sulfation, selective roasting, and water leaching by Önal et al [48] and was provided for the experiments. The leachate composition, pH value and SO_4^{2-} concentration were determined upon receipt. Solvent extraction experiments were performed using D2EHPA (97%, Sigma-Aldrich) diluted in Solvent 70, hexane, octane (98%, reagent grade), toluene, cyclohexanone, 1-octanol, and chloroform ($\geq 99.9\%$, containing amylenes as stabilizer, Sigma-Aldrich) to concentrations of 0.3, 0.6, 0.9, and 1.2 mol/L, with the obtained leachate as the aqueous phase. Extraction kinetics, the effect of D2EHPA concentration and the effect of the diluent were investigated. All the organic phases were pre-equilibrated with an equal amount of MQ water. Shaking was done in 3.5 mL glass vials at 25 ± 1 °C, and an aqueous-to-organic phase ratio, $\Theta = 1$ on an Ika Vibrax Vxr shaking machine at 1750 vibrations/min. All the experiments were performed in triplicate. In all cases the error bars on the graphs were omitted due to lack of graph clarity and insufficient scientific meaning for this specific case. The vials were centrifuged at a rotation speed of 2000 rpm for 1 min before each sampling. The sampled aqueous phases were diluted with 0.5 mol/L HNO_3 and analyzed using ICP-OES. The distribution ratios were calculated as the mass balance of these measurements.

The dependence of the extraction process on the equilibrium pH was also investigated. The organic phase used was 0.3 mol/L D2EHPA in Solvent 70. The pH of the aqueous phase was adjusted by adding small amounts of 0.1 or 3 mol/L NaOH to increase the pH or conc. H_2SO_4 to lower the pH. A specific amount of the organic phase was added to the extraction system, which corresponded to the amount of the NaOH_{aq} or conc. H_2SO_4 added. The equilibration was performed for 20 min by manual shaking before sampling to ensure re-equilibration. The sampled aqueous phases were diluted with 0.5 mol/L HNO_3 and analyzed using ICP-OES.

Stripping was performed by contacting the loaded organic phases with the best extraction properties with 0.5, 1, 1.5, 2, 2.5, and 3 mol/L hydrochloric acid (HCl; 37%, puriss, Sigma-Aldrich). A volume of 5 mL of each of the phases was added into a 20 mL vial and shaken manually for 20 min at a temperature of 25 ± 1 °C and $\Theta = 1$. After the stripping process, the stripping aqueous phases were sampled, diluted with 0.5 mol/L HNO_3 and analyzed using ICP-OES.

More experimental details can be found in [17].

c) Extraction of REEs from organic acids leachates using D2EHPA, TODGA, Cyanex 923, Cyanex 272 and TBP in various diluents

To extract metals from the organic acid leachates, D2EHPA in Solvent 70 was used. D2EHPA is a widely used industrial extracting agent. It was used in the case of 1 mol/L citric, acetic, glycolic and maleic acid leachates to determine the possible use for the recovery of REEs and other elements from organic acids leachates using solvent extraction. Concentrations of 0.2, 0.4, 0.6 and 0.8 mol/L concentrations were used. The experiments were performed on the Ika Vibrax Vxr basic shaking machine in 3.5 mL glass shaking vials for 10 min and the $V_{\text{org}} : V_{\text{aq}} =$

1. After the extraction, the aqueous phase was sampled, diluted in 1 mol/L HNO_3 and measured using the ICP-OES. The equilibrium pH values in the aqueous phase were measured using MeterLab™ PHM 240 pH/ion Meter pH electrode. Further experiments using 1 mol/L TBP (Sigma-Aldrich, 97%), TODGA (synthesized at Chalmers University of Technology, >98%), Cyanex 272 (Cytec, 85%) and Cyanex 923 (Cytec, 93%) were performed on 1 mol/L glycolic and maleic acid leachates.

4.4. Laboratory pilot-scale separation of REEs

Based on previous experiments, 1 mol/L D2EHPA in Solvent 70 and 1 mol/L acetic and citric acid leachates were chosen for a scale-up in the mixer-settler batteries. To be able to apply the system to a mixer-settler battery and for constructing McCabe-Thiele diagrams, the organic phase (1 mol/L D2EHPA in Solvent 70) and aqueous phases (1 mol/L citric acid leachate, pH=2 and 1 M acetic acid leachate, pH=4) were brought into contact for 3 minutes at various O:A ratios (v/v) 4:1, 2:1, 1:1, 1:2, 1:4 and 1:6 in 3.5 mL shaking vials. The temperature was kept at $25 \pm 1^\circ\text{C}$ and the shaking speed was 1500 rpm on an IKA Vibrax shaking machine with custom-made vial holder. Additionally, stripping from the loaded organic phases was performed using 2 mol/L HNO_3 and 2 mol/L HCl (prepared from ACS reagent, 37%), as known efficient stripping agents. Furthermore, 3 mol/L citric acid and 4 mol/L acetic acid were used to determine if there was also any potential for using organic acids as stripping agents, since they were efficient for the leaching process and a process could be developed with only organic acids as the aqueous phase. The loaded organic phase was prepared by manually shaking 1 mol/L D2EHPA in Solvent 70 with either 1 mol/L citric or 1 mol/L acetic acid leachate at O:A ratio 1:2 in a 50 mL PP bottle. Stripping was subsequently carried out with the aforementioned stripping agents at A:O ratios 6:1, 4:1, 2:1, 1:1, 1:2 and 1:4. Temperature was kept at $25 \pm 1^\circ\text{C}$ using a thermostatic bath and the shaking speed was 1500 rpm on an IKA Vibrax shaking machine with custom-made vial holder. Contact time was 1 minute. The choice of contact time was based on the previous kinetics experiments. Mixer-settler batteries with a counter-current flow of organic and aqueous phase were used for the pilot scale experiments. The schematic of the process used is shown in Figure 4.2.

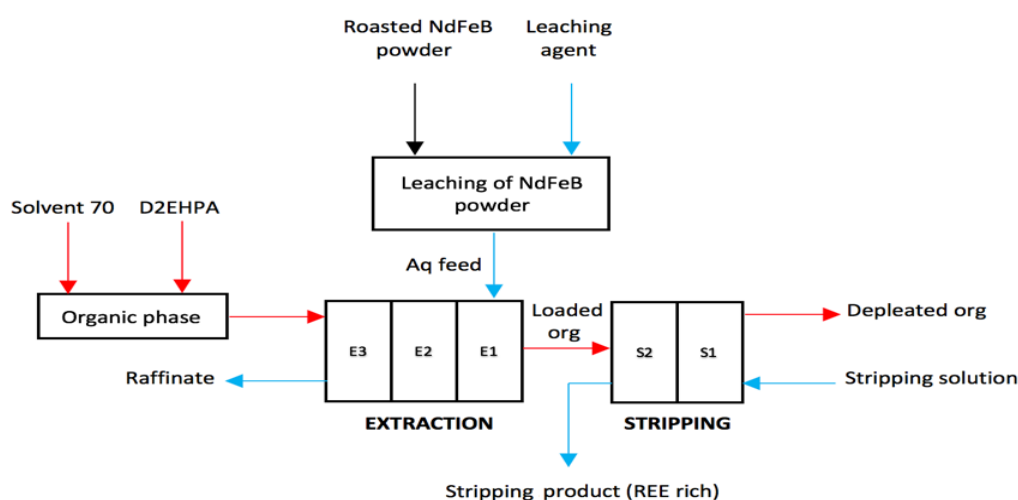


Figure 4.2. Pilot scale scheme for the extraction of REEs from neodymium magnet leachates (1 mol/L acetic and citric acid leachates) using 1 mol/L D2EHPA in Solvent 70.

Up to three stages of extraction were used for the separation of REEs from the leachate, followed by two stages of stripping. Mixer-settler units were made of PVDF (polyvinyl difluoride) with a holdup volume of 120 mL. The flow rates for both aqueous and organic phase were 4 mL/min to ensure disengagement of the phases in the mixer-settler unit. Stirring in the units was done using MSU 0.5 stirrer motor control units with remote stirrers attached and the speed was ca 2000 rpm. Phases were pumped through the system using IWAKI pumps. 1 M citric and 1 M acetic acid leachates were used as aqueous feed and 1 M D2EHPA in Solvent 70 was used as the organic phase feed. The O:A ratio in the solvent extraction step was 1:2, while the A:O ratio in the stripping stage was 1:1. The samples in every stage were taken after 30, 60 and 120 minutes to ensure that equilibrium was reached. Sampling was done in triplicate to ensure reproducibility of the results. Equilibrium pH value in the aqueous phase of every extraction stage was measured using a MeterLab™ PHM 240 pH/ion Meter pH electrode.

5. RESULTS AND DISCUSSION

5.1. Elemental composition of the waste

HD NdFeB is a REE-rich waste fraction (Table 5.1.), which make up more than a quarter of the magnet mass, making it a feasible recycling waste stream for REEs. The most valuable REE in the waste fraction is Nd at around 25 wt%, followed by Pr at 2.6 wt% and Dy at around 1 wt%. The largest constituent of the HD NdFeB was Fe, which makes up around 60% of the waste mass. Other impurities, including Co and B, were also found in wt% around 1%, and Ni (around 2%), which is commonly found in the NdFeB coating [30]. The composition determined here matches the content of the REEs and other constituent elements of the NdFeB magnets found in industrial streams [3-5]. HD NdFeB powder was roasted and demagnetized to potentially increase its leaching properties (particularly in organic acids) and minimize the amount of powder clinging to the stirring magnet. As in the case of HD NdFeB, more than one quarter of the roasted NdFeB powder consists of REEs (Table 5.1.). As expected, the two major components of the roasted neodymium magnet powder were Fe and Nd, making up around 56.4% and around 22.7% of the powder, respectively. Pr made up $2.73 \pm 0.05\%$ and Dy $0.77 \pm 0.01\%$ of the overall composition; percentages that are similar to the ones in the HD NdFeB powder. Some impurities present in the NdFeB magnet structure, such as Co and B, are also present, but in percentages lower than 2%. Fe and Nd are represented in slightly lower percentages than expected, which can be attributed to the reaction of oxygen and other atmospheric gases with the original powder during roasting, since the oven did not have a controlled atmosphere. Ni was not detected in the roasted NdFeB powder due to sieving of larger parts (usually contain Ni). The difference from 100% can also be attributed to experimental errors.

Table 5.1. Elemental composition, in wt%, of a) HD NdFeB totally dissolved in aqua regia for 1 hour at $80 \pm 1^\circ\text{C}$ and S:L = 1 /10 g/mL) and b) roasted NdFeB powder dissolved in aqua regia for approximately 6 hours at a temperature of $23 \pm 1^\circ\text{C}$ and S:L = 0.1 /5 g/mL. There were no residues after filtration.

Element	a) Mass fraction in HD NdFeB magnet powder / wt% [14]	b) Mass fraction in roasted NdFeB magnet powder / wt%
Fe	61.1 ± 1.0	56.4 ± 0.3
Nd	25.3 ± 0.7	22.7 ± 0.0
Pr	2.62 ± 0.17	2.73 ± 0.05
Dy	1.08 ± 0.27	0.77 ± 0.01
Co	1.42 ± 0.07	1.25 ± 0.03
B	1.00 ± 0.02	0.74 ± 0.01
Ni	2.03 ± 0.23	nd
other	~5.45	~15

SEM/EDX was performed in order to examine the morphology changes and the redistributions of elements that occurred to the HD NdFeB powder during roasting and sieving. Figure 5.1 shows the SEM and EDX of the HD NdFeB powder (a and b) and the roasted NdFeB powder (c and d).

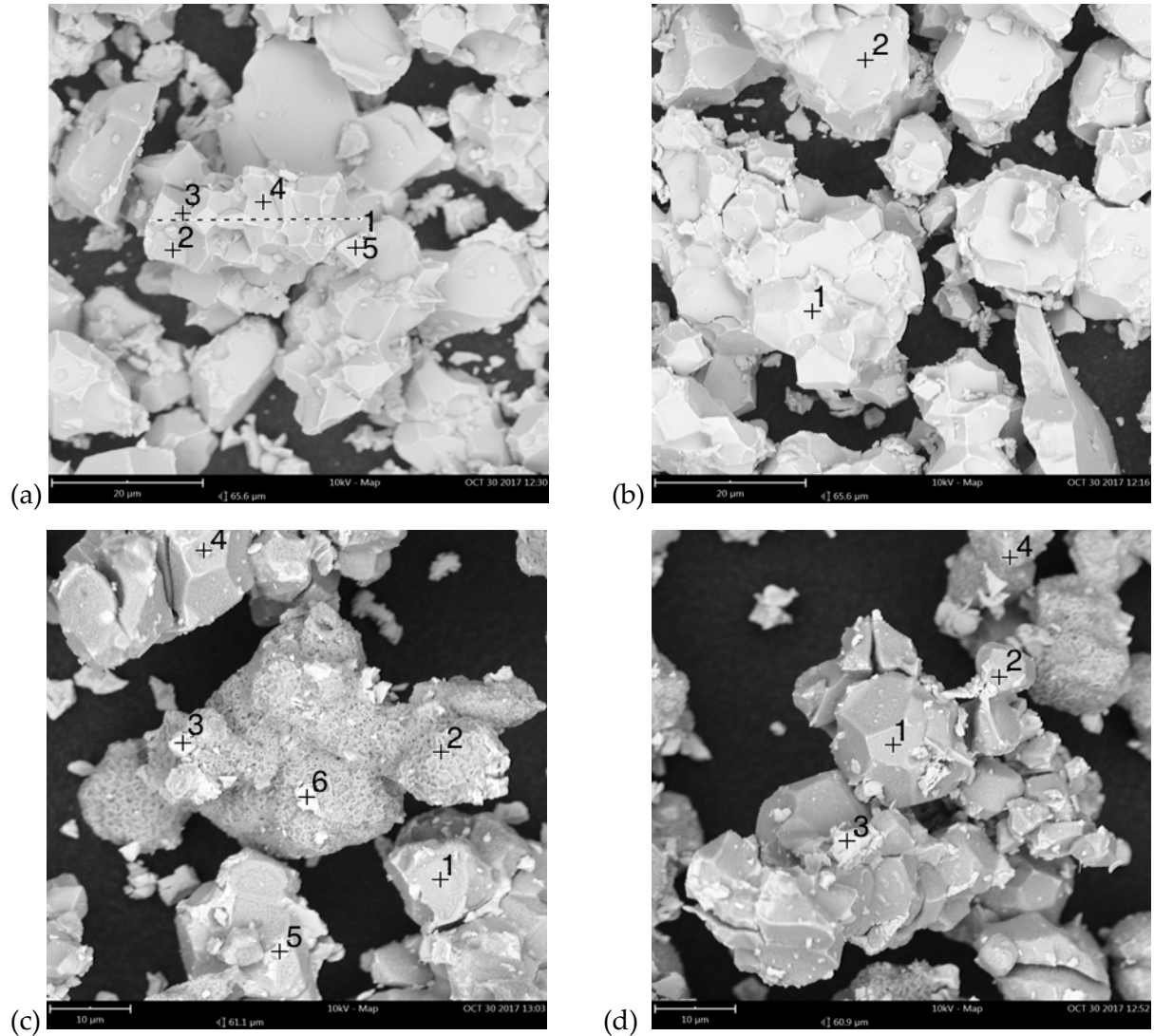


Figure 5.1. Four different SEM magnifications (4100 x, 10 kV - Map) HD NdFeB powder in two different locations a) and b) and roasted neodymium magnet powder sample in two locations c) and d). The crosses and lines on the SEM pictures show the locations where the EDX analysis was performed.

In Figure 5.1 a) and b) it can be seen that particles have similar morphology, while particle sizes vary between 2-20 μm . The elemental composition of HD NdFeB powder, according to EDX analysis results, is similar to the composition of other NdFeB magnets found on the market. [5] Parts of the powder, such as the one represented by Line 1 in Figure 5.1.(a) and point 2 in Figure 5.1.(b) show higher amounts of oxygen. This can be attributed to the fact that the REE-rich grain boundary phase oxidizes fast when exposed to air during the HD process [87], but overall no elemental clustering was observed. The SEM/EDX analysis of the roasted NdFeB powder (Figure 5.1. (c) and (d)), shows diverse morphology. Various particles, including mainly the flat surface particles sized around 10 μm in diameter, the bulkier particles with a distinct rugged morphology with diameter sizes of around 10-20 μm , and small white

specks less than 5 μm in diameter can be observed. EDX indicates that the flat surface particles are largely composed of Fe and O (spots 1 and 2 in Figure 5.1. (d)), and the white specs consisted mainly of Nd, Pr and O, pointing to the creation of clusters of REE- oxides during the roasting treatment. The large particles with the rugged surface consisted mostly of Fe and O and smaller amounts of REEs. The weight percentage fluctuations are probably due to variations in the penetration depth of the electrons during the EDX analysis, which can vary depending on the surface topography and composition. Since the electrons penetrate at an approximately constant mass, spatial resolution is a function of density.

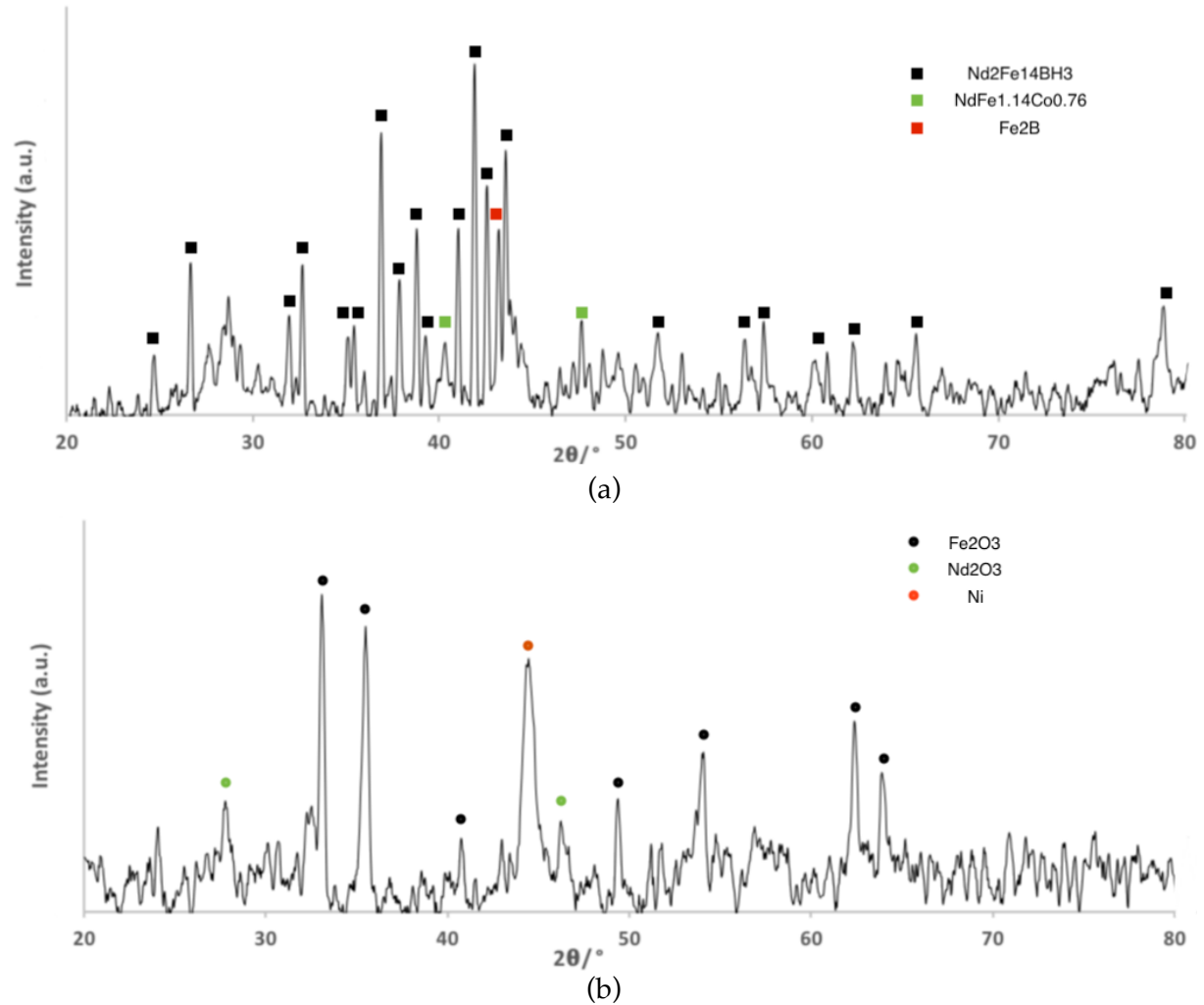


Figure 5.2. XRD pattern of a) hydrogen decrepitated NdFeB powder and b) roasted NdFeB powder.

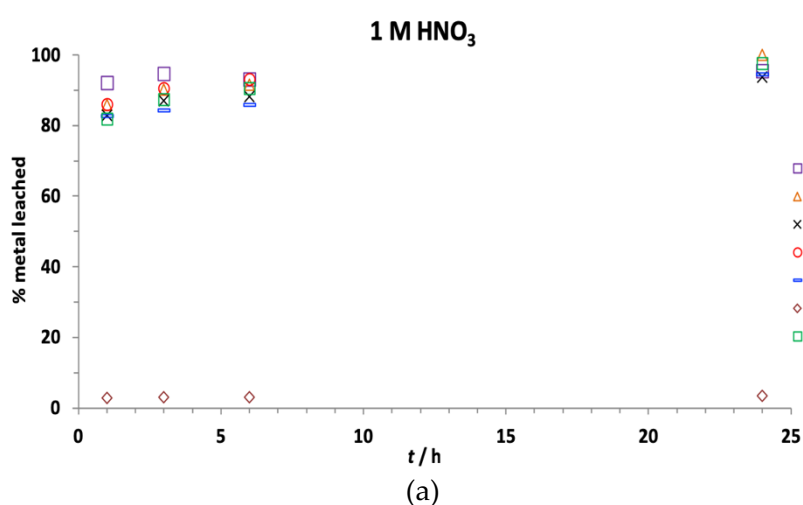
Both powders were analyzed using XRD to further determine their crystalline composition. The XRD pattern of the HD NdFeB powder (Figure 5.2. a)) showed the presence of $\text{Nd}_2\text{Fe}_{14}\text{BH}_3$, a hydride formed during the hydrogen decrepitation process. Apart from the main $\text{Nd}_2\text{Fe}_{14}\text{BH}_3$, the presence of Fe_2B and $\text{NdFe}_{1.14}\text{Co}_{0.76}$ was observed. The XRD pattern also showed the presence of traces of Ni. The XRD pattern of the roasted NdFeB powder (Figure 5.2. b)) showed the presence of Fe_2O_3 and Nd_2O_3 , formed during the roasting process in the presence of air. Ni is also present in high amounts in elemental form. Apart from these main components there were also traces of Pr_2O_3 and Fe in elemental form. The results of the XRD correlated well with the results of the SEM-EDX analysis.

5.2. Leaching out the REEs from waste

Overview of the leaching results, as well as a comparison between using inorganic and organic acids when leaching the waste as previously described.

5.2.1. Leaching using inorganic acids

In Figure 5.3 the results of leaching of HD NdFeB powder using 1 mol/L HNO_3 , 1 mol/L HCl , 1 mol/L H_2SO_4 and 1 mol/L $\text{CH}_3\text{SO}_3\text{H}$ are presented. Inorganic acids proved to be very efficient in leaching out of REEs from the powder. It was observed that the leaching time played a role in the leaching process, although this was not as significant since most of the REEs (over 80%) were leached after 1 h and reached over 90% after 3 h leaching time. All of the REEs were completely leached after 24 h in all acids used. The efficiency of 1 M acids in the leaching of REEs decreases in the following order $\text{H}_2\text{SO}_4 > \text{HCl} > \text{HNO}_3 > \text{CH}_3\text{SO}_3\text{H}$, which correlates with their pK_a values and the fact that H_2SO_4 dissociates in 2 steps to produce 2 H^+ ions (the pK_{a2} is lower than that of all the organic acids tested in this work). Increasing the concentration of the acids up to 3 M did not result in significant increase in the amount of leached REEs. An important observation was that in the case of 3 mol/L HNO_3 , 3 mol/L HCl and 3 mol/L H_2SO_4 , adding the powder into the lixiviant caused a vigorous reaction with the powder, with evolution of NO_2 in the case of HNO_3 due to high oxidizing conditions and an exothermic reaction. Similar effects have been noticed in previous research [45], suggesting roasting as a solution to this problem that would also lead to less heat release and less gas evolution during the leaching of oxides. Alongside REEs, other constituent elements of the NdFeB magnet were also co-leached using all of the acids mentioned and no selectivity was achieved between REEs and B, Co and Fe. Ni, however, was not leached using either of the acids. It can be seen in Figure 5.3 that low amounts of Ni were leached after 24 h (less than 20% in 1 mol/L HCl and 1 mol/L H_2SO_4 and less than 5% 1 mol/L $\text{CH}_3\text{SO}_3\text{H}$ and 1 M HNO_3), which was expected since Ni is added to the coating that protects NdFeB magnets from corrosion [30].



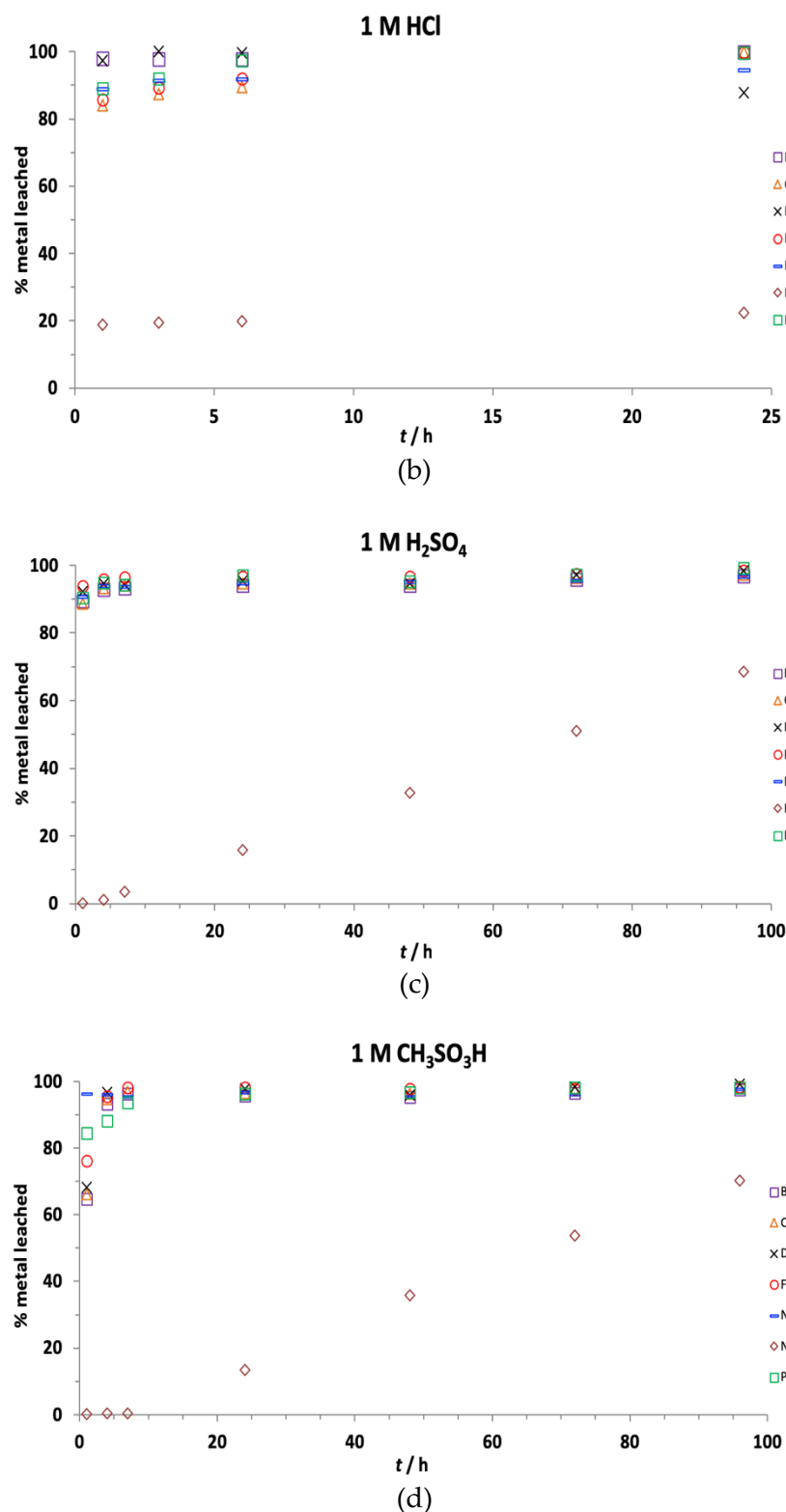


Figure 5.3. Effect of 1 M (a) HNO₃, (b) HCl, (c) H₂SO₄ and (d) CH₃SO₃H and leaching time (1–168 h) on the leaching efficiency of B, Co, Dy, Fe, Nd, Ni and Pr. The temperature was kept at 25 ± 1°C, magnetic stirring at 400 rpm and S:L ratio at 1/50 g/mL.

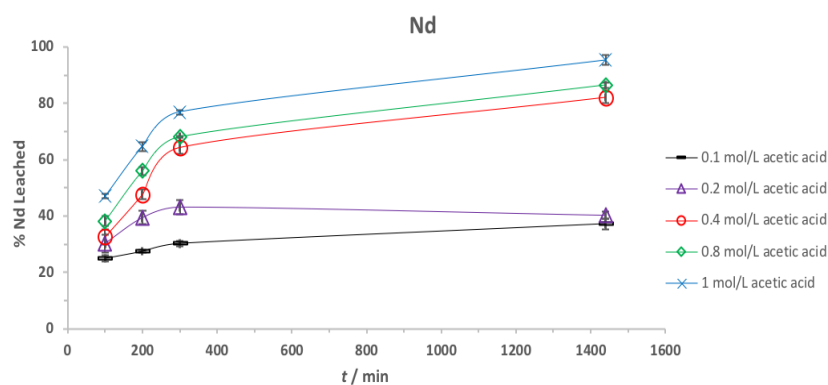
5.2.2. Leaching using organic acids

HD NdFeB powder was leached using 0.4–1.6 mol/L citric acid and acetic acid. S:L ratio was kept at 1/50 g/mL and leaching temperature was 25 ± 1 °C. The leaching kinetics of REEs were found to be very slow. Less than 20% of the REEs were dissolved after 8 hours, even at concentrations above 1.2 mol/L. To leach 80% of Nd and 60% of Pr and a mere 20% of Dy around 5 days were needed. Thus, the HD NdFeB powder was roasted and demagnetized to potentially increase its leaching properties since this was done in previous works [45-47]. Roasting was used to change the powder chemically and demagnetization minimized the amount of powder clinging to the stirring magnet. The organic acids used for leaching of roasted NdFeB powder were citric acid, acetic acid, maleic acid, glycolic acid and ascorbic acid. They all showed good leaching properties for REEs out of the roasted NdFeB powder and their leaching properties will be further discussed in this section.

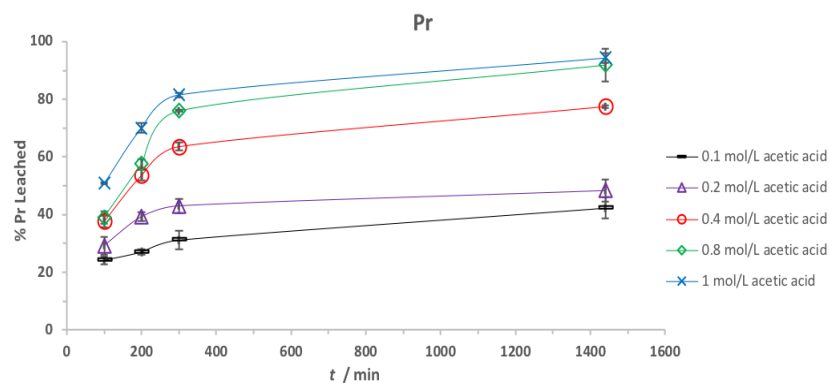
Leaching behavior of roasted NdFeB powder in acetic and citric are presented in Figure 5.4 and Figure 5.5, respectively. Each point on the kinetic curve representing the % of REEs, Fe, and Co leached is represented as an average of a triplicate experiment.

Acetic acid

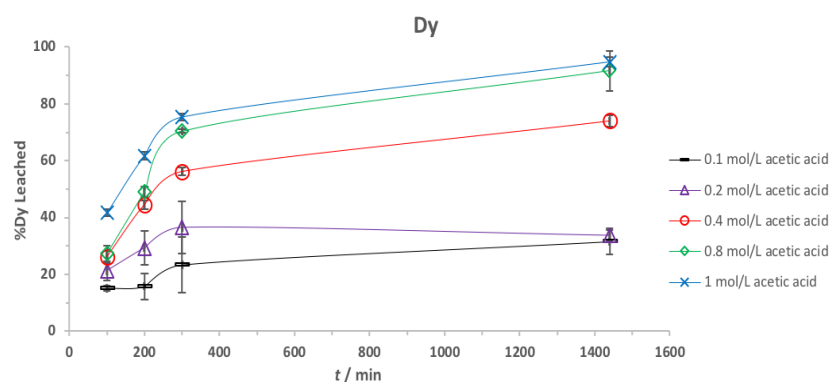
Various concentrations of acetic acid were investigated in the leaching of Nd, Pr, Dy, Fe, Co, and B with variation of the leaching time from 0–24 h, temperature at 25 ± 1 °C and S:L ratio of 1/50 g/mL. Acid concentration and leaching time have played an important role in the leaching efficiency of REEs and other elements from the roasted NdFeB powder. Varying the acetic acid concentration from 0.05 to 1 mol/L at 24 h leaching time increased the leaching efficiency from <20% to >95% for all REEs. Thus, acetic acid in concentrations higher than 1 mol/L is recommended for efficient recovery of REEs from roasted neodymium magnet powder. After 24 h of leaching with 1 mol/L acetic acid, almost all of the Dy, Pr, Fe, Co, and B had leached into the solution, while over 95% of Nd was recovered. Diluting acetic acid from 1 mol/L to 0.1 mol/L decreased the pH value from 2.2 to 2.8. The pH values of the leachates after 24 h leaching were 4.1, 4.2, 4.6, 5.2, 5.6, and 5.9 for 1 mol/L, 0.8 mol/L, 0.6 mol/L, 0.4 mol/L, 0.2 mol/L, and 0.1 mol/L leachates, respectively, pointing to proton starvation during leaching. No selectivity between the leaching efficiency of REEs and other elements was observed, since the leaching efficiency of the REEs was similar to those of Fe, B, and Co. As 1 mol/L acetic acid was needed for quantitative leaching of REEs, this concentration was used for further experiments.



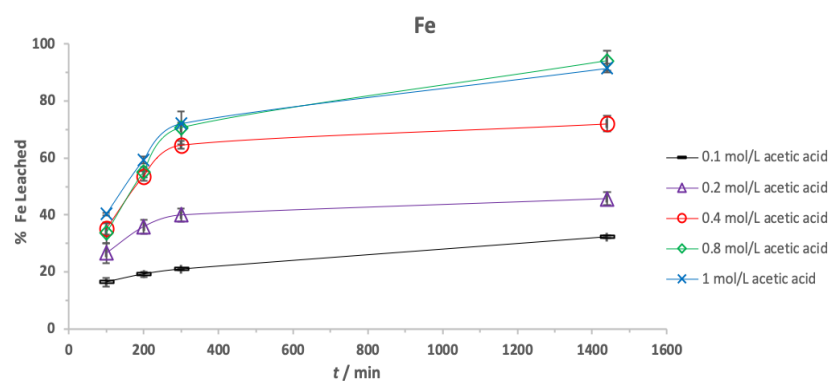
(a)



(b)



(c)



(d)

Figure 5.4. Effect of the concentration of acetic acid (0.1, 0.2, 0.4, 0.8 and 1 mol/L) and leaching time (100 min, 200 min, 300 min and 24 h) on the leaching efficiency of a) Nd, b) Pr, c) Dy and d) Fe. The temperature was kept at $25 \pm 1^\circ\text{C}$, magnetic stirring at 400 rpm and S:L ratio at 1/50 g/mL.

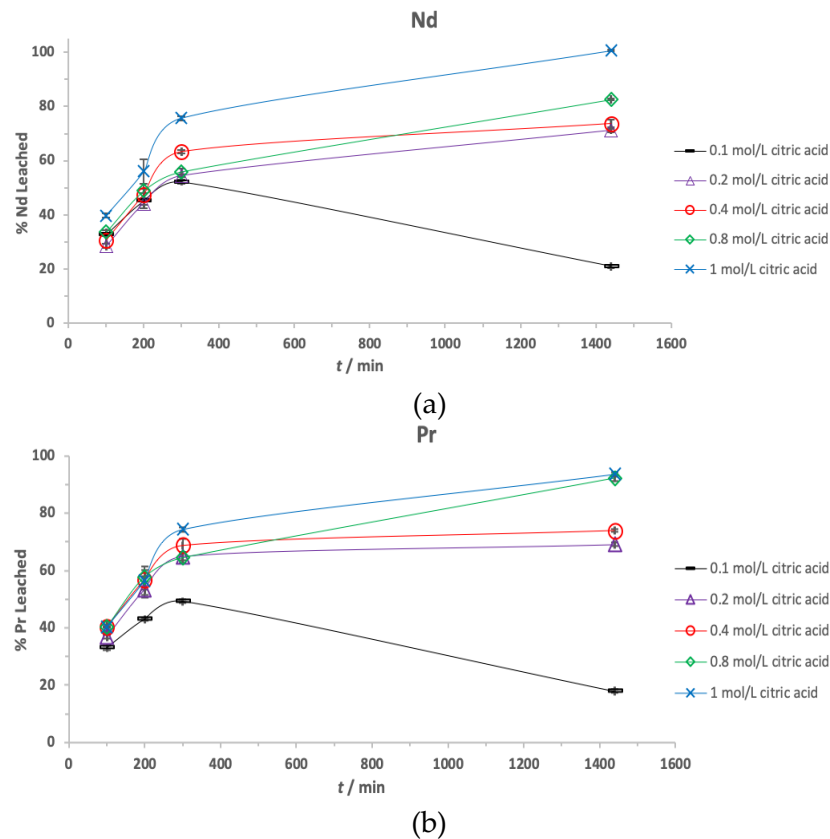
Citric acid

As in the case of acetic acid, varying the concentration of citric acid influenced the leaching efficiency of the elements from the roasted NdFeB powder (Figure 5.5). Increasing the concentration of citric acid from 0.1 mol/L to 1 mol/L effected the leaching efficiency for the REEs. This increased from <20% to >95%, with the highest value reached after 24 h. No selectivity in the leaching of REEs and other elements in the powder was observed since the increase in the leaching efficiency of REEs was accompanied by the co-leaching of Fe, B, and Co into the solution. The pH value of the leaching acid increased from 1.23 to 2.5 from

1 mol/L to 0.1 mol/L, while the values after 24 h leaching were 2.3, 2.6, 3.4, 4.5, and 5.3 for 1 mol/L, 0.8 mol/L, 0.6 mol/L, 0.4 mol/L, 0.2 mol/L, and 0.1 mol/L of citric acid, respectively.

The decrease in leaching efficiency of the Nd, Pr, and Dy that occurred after 24 h leaching with 0.1 mol/L citric acid was especially interesting since Fe and Co did not exhibit the same behavior. This can be explained by the pH increase up to 5.3 in the 0.1 mol/L, which led to precipitation of the REEs, most likely as citrates. Citrates of REEs are known to be soluble in aqueous solutions around pH 2–5 [75].

Both acetic acid and citric acid showed much better leaching properties when the roasted and sieved NdFeB powder was used than was the case for the HD NdFeB magnet waste. It was shown that roasting and the elemental redistributions that occurred during the process (molar volume changes during the oxidation and pore formation that make the inner surfaces of the powder more available for leaching) benefited the leaching properties. Sieving the powder into smaller particles also improved the leaching process, which was also shown in a previous work by Behera et al. [19]. The ideal conditions for the leaching of Nd were determined to be 1 mol/L of either citric or acetic acid, and further experiments were conducted with these concentrations.



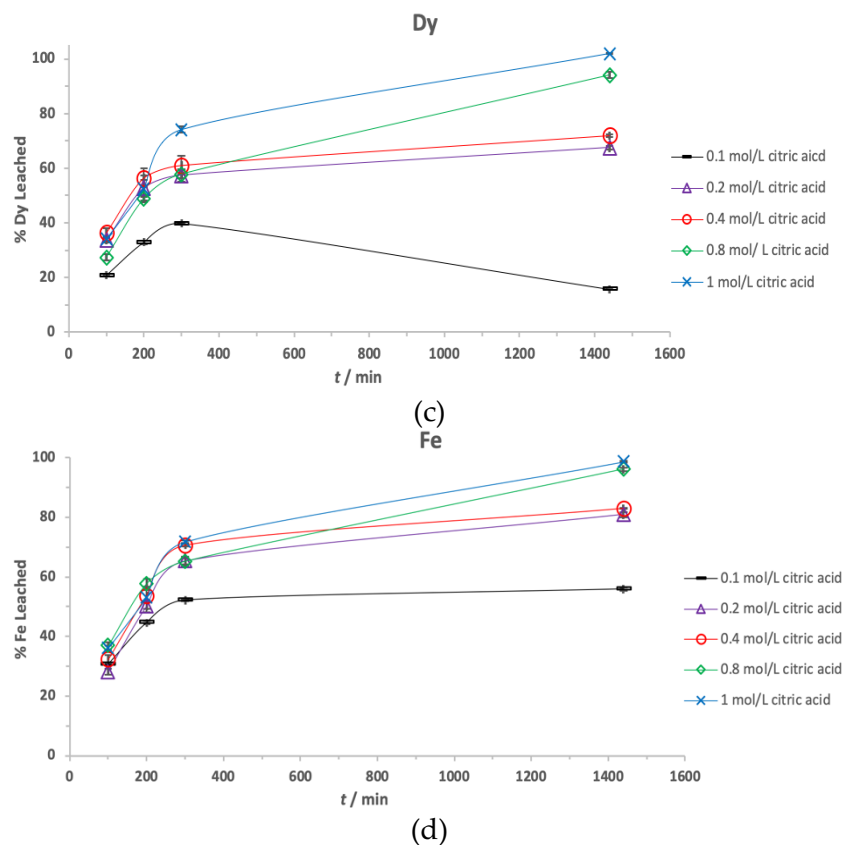


Figure 5.5. Effect of the concentration of citric acid (0.1, 0.2, 0.4, 0.8 and 1 mol/L) and leaching time (100 min, 200 min, 300 min and 24 h) on the leaching efficiency of a) Nd, b) Pr, c) Dy, d) Fe and e) Co. The temperature was kept at 25 ± 1 °C, magnetic stirring at 400 rpm and S:L ratio at 1/50 g/mL.

Comparison between acetic and citric acids

The amounts of leached Nd, Pr, Dy, Fe and Co using 1 mol/L citric and acetic acid are shown in Figure 5.6. Varying the S:L ratios from 1/30 to 1/50 g/mL was tested. In 1 mol/L citric acid the variation of S:L had negligible effects on the leaching efficiencies of all the elements present. Dy showed slightly higher leaching efficiency at 1/80 S:L ratio, but all within a margin of statistical error. Varying the S:L ratio from 1/30 to 1/80 g/mL for leaching with 1 mol/L acetic acid did not affect the leaching efficiency of Nd, Pr, and Dy, which stayed the same across the S:L ratio. However, it had a significant effect on the leaching of Fe, which was leached at $61.69 \pm 6.58\%$ at 1/30 g/mL and $79.30 \pm 2.28\%$ at 1/80 g/mL. This can be attributed to the dissociation constants of the acids. Acetic acid is a monoprotic acid with $pK_a = 4.76$, while citric acid is a triprotic acid with $pK_{a1} = 3.13$, $pK_{a2} = 4.76$ and $pK_{a3} = 6.39$, which can explain why the leaching efficiency of Fe was lower due to proton starvation in the acetic acid leachate, since Fe is present in such high amounts. Exact amounts of H^+ were not recalculated from the pK_a values as activity coefficients would need to be determined in that case. The leaching of Co was also affected by the variation of S:L ratio. Co leaching increased from $86.11 \pm 0.38\%$ at 1/30 g/mL to $93.92 \pm 1.70\%$ at 1/80 g/mL. For removal of Co from the leachate Cyanex 272 can be used on an industrial scale at equilibrium pH 4–5 [88]. Boron was leached quantitatively at all S/L ratios investigated. For complete extraction of B from the leachate, aliphatic 1,3-diols can be used [89].

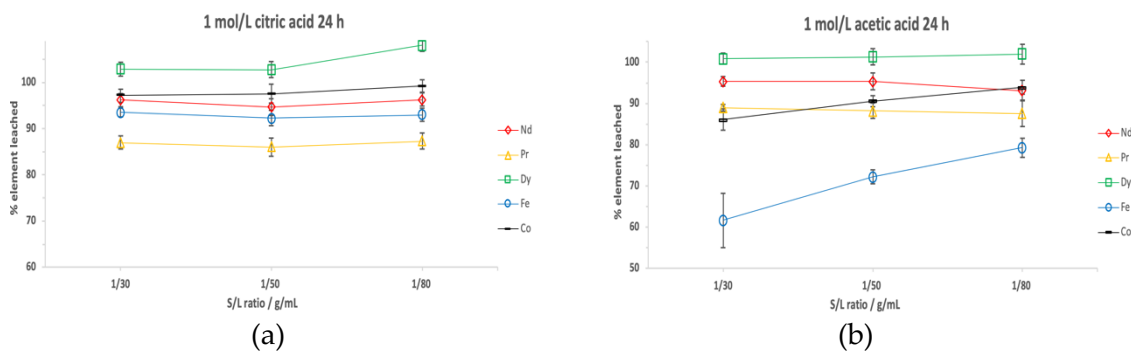


Figure 5.6. The dependence of the amount of Nd leached on the S:L ratio at 25 ± 1 °C, using (a) 1 mol/L citric acid and (b) 1 mol/L acetic acid with 400 rpm stirring for 24 h in both cases.

Glycolic, maleic and ascorbic acids

The leaching behavior of the roasted NdFeB powder in glycolic, maleic and ascorbic acid was studied at constant temperature and S:L ratio (25 ± 1 °C and 1/50 g/mL) while the acid concentrations were varied from 0.6 mol/L to 1 mol/L. The results are shown in Figure 5.7. The leaching efficiency increased with the increasing acid concentration. The equilibrium was reached after 400 minutes in glycolic and maleic acids and remained unchanged after 24 hours, which is why the 400 minute duration was used in further studies concerning maleic and glycolic acid. For ascorbic acid, however, the equilibrium was not reached within 24 h and concentrations remained significantly lower than for the other acids. The acid concentration 1 mol/L proved to be the most efficient in the leaching process and this was used in further studies. The influence of acid concentration can be explained by the drop in pH and rise of the acidity of the solution, allowing better conditions to dissolve REEs and other metals due to higher amounts of H^+ ions to attack the elements in the roasted magnet. The leaching efficiencies decrease in the following order maleic acid > glycolic acid > ascorbic acid. Ascorbic was the weakest of all 3 acids, therefore the leaching efficiency seems to correlate with the pKa ranking of the acids. Other elements analyzed (Fe, Co and B) were efficiently dissolved with maleic and glycolic acids (between 80 and 90% at 1 mol/L after 400 minutes). This is good and equivalent to some inorganic acid leaching and can be improved by optimizing different conditions, such as temperature and S/L ratio. The pH of the acids before leaching was measured and determined to be around 1 in maleic acid (0.6– 1 mol/L), around 2 in glycolic acid (0.6–1 mol/L) and around 2.2 in ascorbic acid (0.6– 1 mol/L). The pH showed only slight variations (± 0.1) when altering the acid concentration. The pH of the most efficient acid concentrations (1 mol/L) after leaching were measured after filtration and determined to be around 3.5, 4 and 4.5 in maleic, glycolic and ascorbic acid, respectively. The pH increase could explain the slight loss of leaching efficiency of Fe and REEs in glycolic and maleic acid, since some precipitation or suspension of precipitate might have occurred in the system.

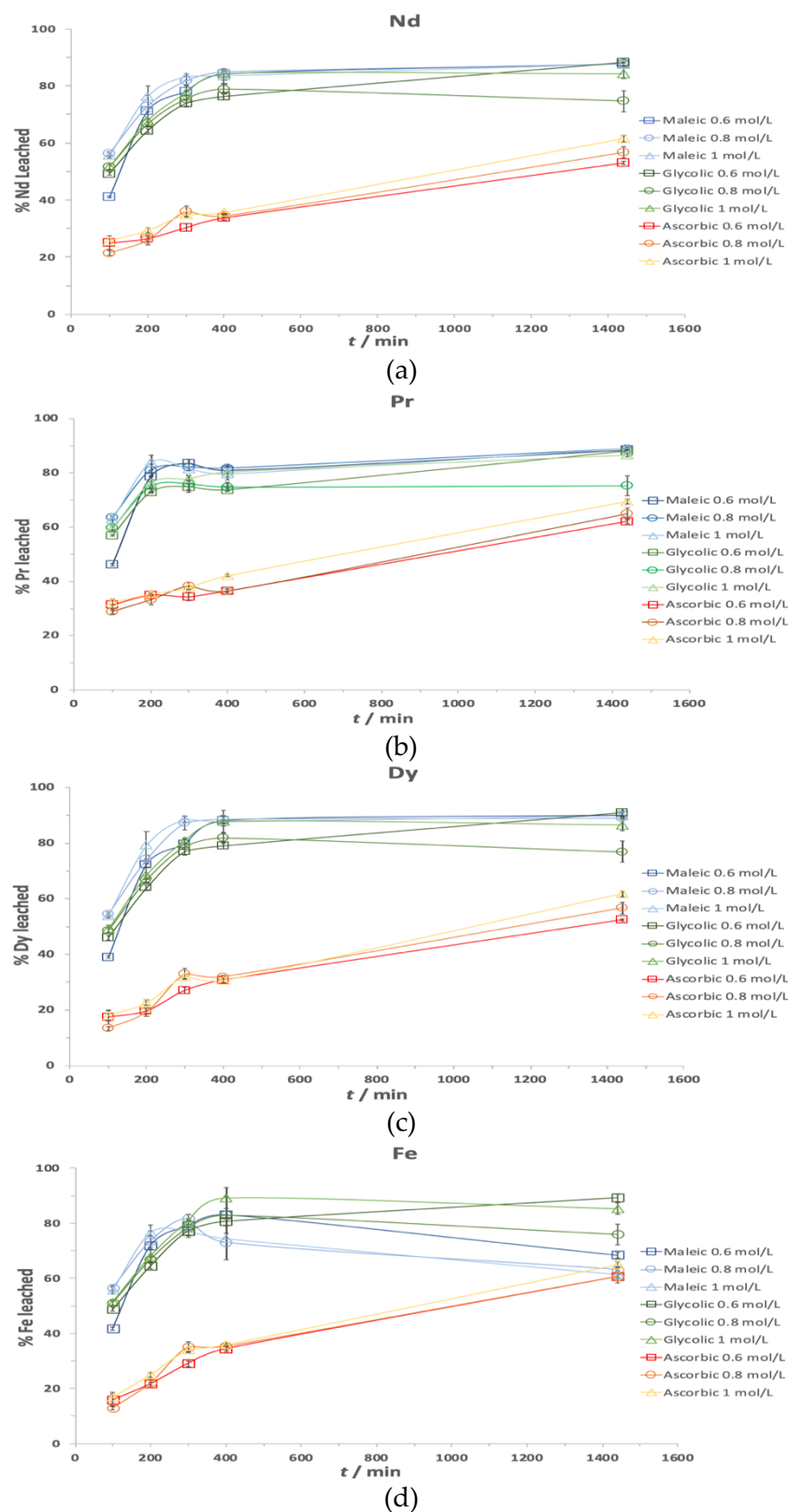


Figure 5.7. Efficiency of leaching with different acids (glycolic, maleic and ascorbic) and acid concentrations (0.6 mol/L, 0.8 mol/L and 1 mol/L), after 100, 200, 300, 400 minutes and 24 hours, in percentages of total (a) Nd, (b) Pr, (c) Dy and (d) Fe dissolved in the solution. Temperature was kept at 25 ± 1 °C, solid/liquid ratio was 1/50 g/mL and stirring speed was 400 rpm.

Based on previous results, the influence of S:L ratio on the leaching was investigated using 1 mol/L glycolic, maleic and ascorbic acid at 25 ± 1 °C varying the S:L ratio from 1/30 g/mL to 1/80 g/mL (Figure 5.8.). It has been shown by other scientific groups that decreasing the S:L ratio increases the leaching efficiencies, since there is more liquid to dissolve the metal compounds in the solid. The results were in correlation with this, since Nd recovery increased from 41% (1/30) to 50% (1/80) in ascorbic acid. Dissolution can be as high as 95% for the S/L ratio of 1/80 g/mL in glycolic acid, which shows the importance of this criterion, allowing leaching with organic acids to reach completion and resulting in release values usually obtained when leaching with inorganic acids.

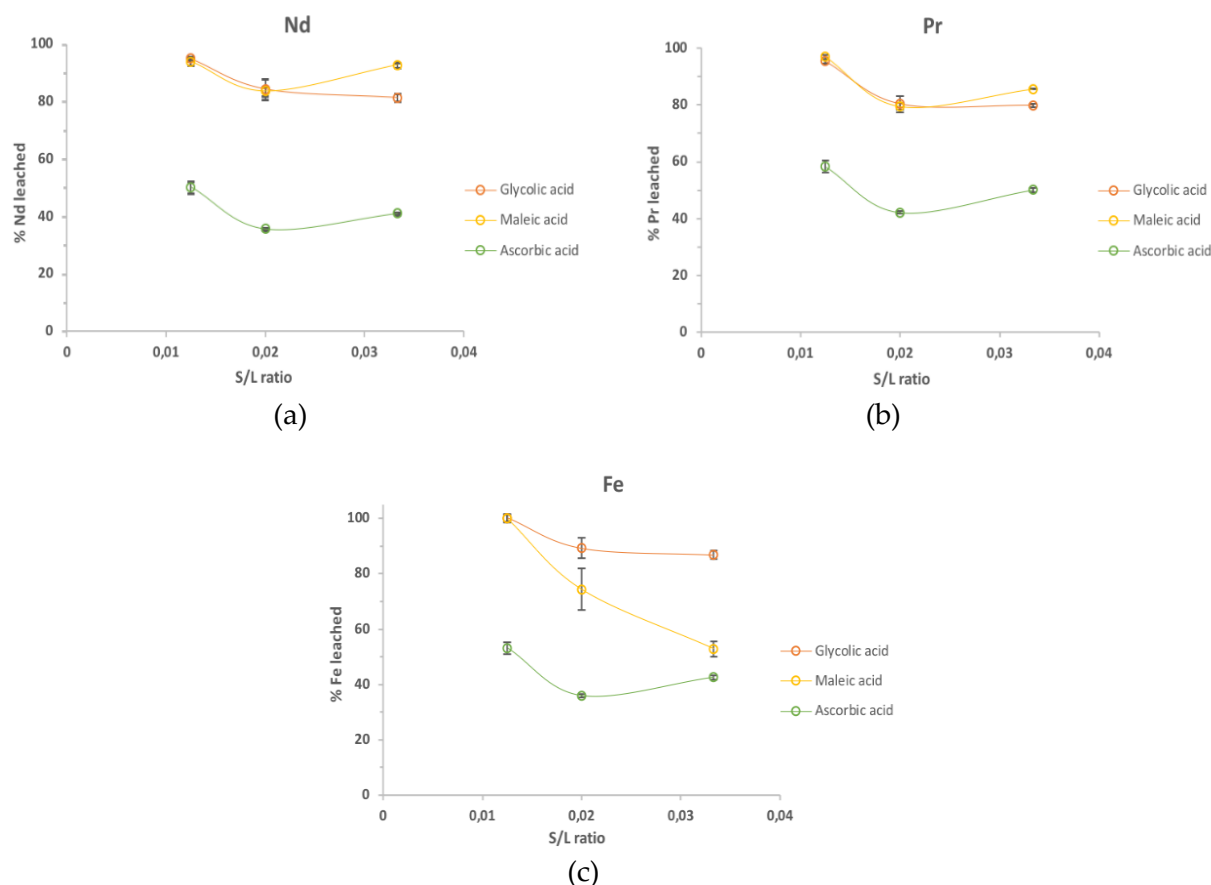


Figure 5.8. Efficiency of leaching with different acids (glycolic, maleic and ascorbic) at different solid/liquid ratios (1/80, 1/50 and 1/30 g/mL), after 400 minutes, shown as percentages of total a) Nd, b) Pr and c) Fe dissolved in the solution. Temperature was kept at 25 ± 1 °C, concentration was 1 M and stirring speed was 400 rpm.

After the determination of the ideal S:L ratios, the temperature effect on the leaching was studied at room temperature (25 ± 1 °C), and then at 50 ± 1 °C and 70 ± 1 °C (Figure 5.9). The concentration of the acid was kept at 1 mol/L and the S:L ratio at 1/80 g/mL. High temperatures usually make species more soluble, as this provides energy to break the bonds (ionic, covalent) between molecules and atoms, leading to solvation of the formed ions. According to other researchers, metal leaching reactions are largely endothermic and are favored by high temperatures that shift the equilibrium in favor of dissolution [19, 45]. The main problem is that all elements in the roasted neodymium magnets follow this trend, so the dissolution rates of Fe and other unwanted elements also rise as temperature increases. In maleic acid, very

little change was observed since the conditions already allowed >90% leaching at room temperature, although with increasing temperature the leaching efficiency did slightly rise for Nd, Pr and Fe. Other elements were leached quantitatively. The largest increase in efficiency was observed in ascorbic acid, where the leaching efficiency of Nd increased from 50% at room temperature to 95% at 70 ± 1 °C, and this rise was observed for all elements measured. In these experiments, optimizing the temperature was the only action identified that allowed ascorbic leaching to reach 90% leaching efficiency. In the case of glycolic acid the opposite trend was observed, as efficiency decreased significantly with increasing temperature. This phenomenon could be explained by the low boiling point of glycolic acid [90] at which decomposition occurs. With this decomposition and volume loss, the strength of the solution diminished and leaching was less efficient. For these reasons, further experiments will be performed at room temperature for leaching with glycolic and maleic acid and it is advised to heat to 70 °C for ascorbic acid use.

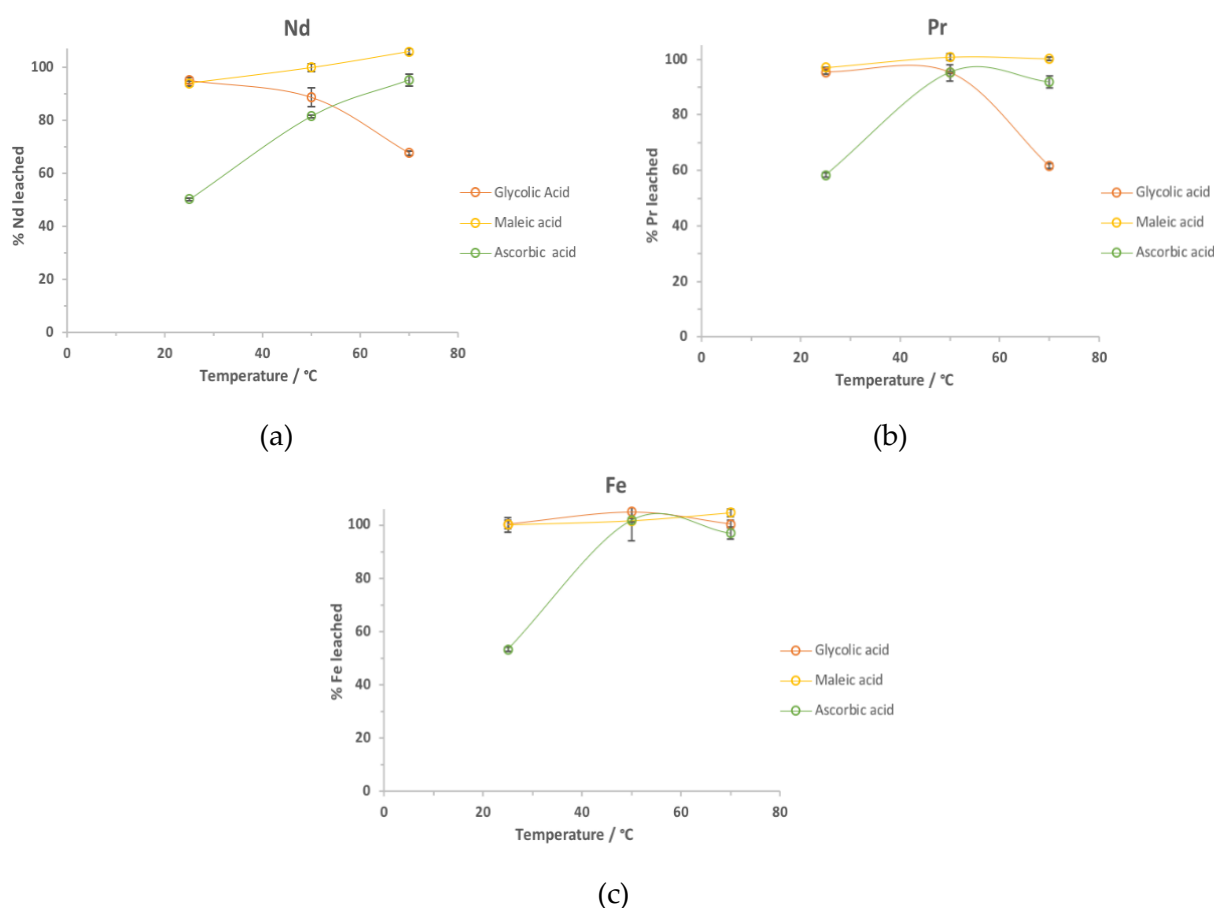


Figure 5.9. Efficiency of leaching with different temperatures (25, 50 and 75 °C), shown as percentage of total a) Nd, b) Pr and c) Fe leached. The solid/liquid ratio was kept at 1/80 g/mL, the stirring speed was 400 rpm, and samples were collected after 400 minutes.

The stirring rate effect of the leaching process was investigated at 1 mol/L, 1/80 g/mL, 400 minutes and 25 °C with glycolic, maleic and ascorbic acid solutions and roasted NdFeB magnet powder. At low rotation speeds leaching can be restricted by matter transfer, since the particles stick to the stirring magnet, so speeds were varied between 400, 700 and 1000 rpm to see if

such limitations could occur. The results showed that 400 rpm was enough, since no significant changes were observed between the investigated samples.

After the leaching experiments were performed, small particles were noticed on the lixiviant surface. This was determined to be mostly Ni from the coating, with admixtures of other elements present in the magnet that were not dissolved regardless of the experimental conditions. [14] Some glycolic acid filtrates, after being left for more than 2 days, started to precipitate. Precipitation mostly occurred in weaker acidic conditions, for example, at 0.6 mol/L and at 1/30 g/mL solid/liquid ratio (pH between 4 - 4.5). These residues were filtered off and dried. They were easily dissolved in 1 mol/L HCl and analyzed by ICP-OES. The analysis of the composition showed that it contained proportionately around twice as much Fe as the magnet material did, in comparison to other metals, such as Nd. Co was also present in high quantities. This was further analyzed by XRD and SEM (Figure 5.10. and Table 5.2.). The microscopic structure of the precipitate can be observed in the SEM image. It consists mostly of large particles containing mainly Fe and O, and locally dispersed smaller shards of Nd. Other elements were not detected as they were present in too small quantities. XRD analysis was inconclusive, due to the high amounts of different species and organic molecules. Traces of glycolates, such as neodymium glycolate, were found.

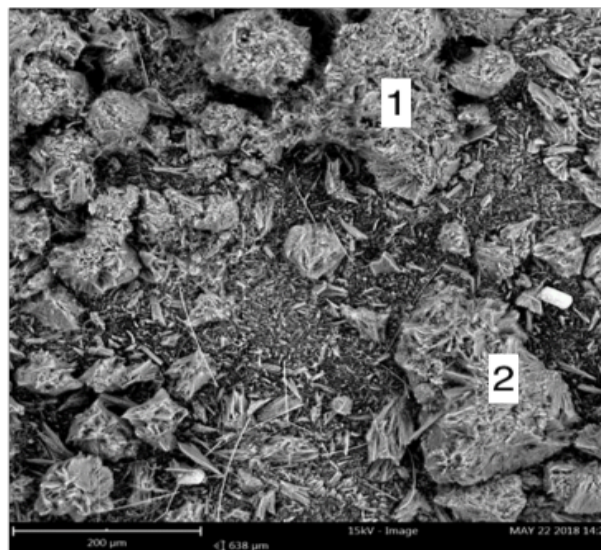


Figure 5.10. SEM magnification (4100 x, 10 kV - Map) of the filtered residues after leaching of the roasted NdFeB powder with 0.6 mol/L glycolic acid for over 24 hours. The spots 1 and 2 in the image show the locations where the EDS analysis was performed.

Table 5.2. Compositions of filtered residues (in wt%) after leaching of roasted NdFeB powder with 0.6 mol/L glycolic acid at 1/30 g/mL, S/L ratio determined by EDX. The positions of the scanned points are shown in Figure 5.10.

Scanned point	w(Nd) / %	w(Fe) / %	w(O) / %	w(Pr) / %	w(C) / %
1	-	29	67	-	4
2	67	33	-	-	-

5.3. Solvent extraction of REEs out from the leachates; diluent effect

The solvent extraction recovery of REEs in this work can be divided into two pathways:

(a) recovery of REEs from inorganic acids leachates (SO_4^{2-} and NO_3^- media) using D2EHPA and TODGA.

(b) recovery of REEs from organic acids leachates (acetic, citric, glycolic and maleic media) using D2EHPA, TODGA, TBP, Cyanex 272 and Cyanex 923.

These are presented in the following subchapters.

5.3.1. Extraction of REEs from HNO_3 leachate using TODGA in various diluents

Since TODGA is known to extract REEs from NO_3^- media with high distribution ratios [68], and HNO_3 was shown to be a good leaching agent for NdFeB waste (Section 5.2.1.), HNO_3 was used as leaching agent for the HD NdFeB powder (composition in Table 5.1). Leaching was efficient with 4 M HNO_3 for 24 h at room temperature and 1/50 g/mL. The filtered residues showed that only Ni was present, which was expected since Ni is used in NdFeB protective coatings. A model solution was used to test the amount of NO_3^- counter-ions needed for efficient extraction with 0.1 M TODGA in Solvent 70, as TODGA is a solvating extractant and the extraction will be governed by the counter-ion concentration, as shown in Equation 3.16. The model solution used contained 21.49 mM Fe, 3.46 mM Nd and 0.62 mM in 0.1 -6 M HNO_3 to represent a NdFeB leachate. After solvent extraction it was determined (Figure 5.11) that a concentration of NO_3^- higher than 2 M was needed for efficient complex formation and achieving the highest distribution ratios for REEs [14].

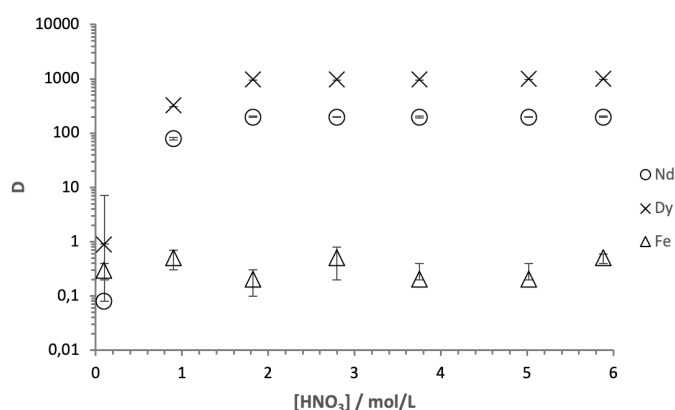


Figure 5.11. The dependence of the distribution ratios of Fe, Nd, and Dy in 0.1 M TODGA in Solvent 70 on initial HNO_3 concentrations of 0.1, 1, 2, 3, 4, 5, and 6 M in the aqueous phase. The temperature was kept at 25 ± 1 °C and the organic-to-aqueous phase ratio was 1:1.

Before the solvent extraction experiments, the filtered leachate was diluted with 3 M HNO_3 to get 4000 mg/L of the powder dissolved. The results of the solvent extraction experiments are presented in Figure 5.12. As expected, the distribution ratios for Nd, Pr, and Dy increase with the TODGA concentration. This was true in all the diluents used, reaching values up to

1000 at the highest TODGA concentrations. The distribution ratios of REEs generally decrease in the following order: hexane > cyclohexanone > Solvent 70 > toluene > 1-octanol. The polarity of the diluents obviously played a big role in their extraction mechanism, since the distribution ratios of the extractable species generally decrease with the polarity of the diluents. Cyclohexanone was an exception, as it has an active oxygen donor atom that has the ability to form complexes soluble in the organic phase [91], which is most likely the reason for achieving higher distribution ratios in this particular diluent. TODGA showed high selectivity of extraction of the REEs. It was observed that the distribution ratios for the heavy REE Dy were higher than those for the light REEs, which can be attributed to higher charge density of the heavy REEs due to smaller ionic radii, which facilitates complex formation. Strong oxygen donor atoms in the TODGA molecule and the size of the diglycolamide group were the reasons for the very high REEs distribution ratios. Due to organic phase saturation at low TODGA concentration, the slope analysis was compromised. Slope analysis, which can only be done when the metal concentration is negligible compared to the TODGA concentration, is most efficiently done with radio tracers. Nonetheless, from the plotted graphs it can be concluded that 2-3 TODGA molecules are involved in complex formation with the REEs, although XAFS analysis would be necessary to get a clearer picture of the chemical structure of the complexes formed. Other relevant studies in the field suggest 3 TODGA molecules are involved in complex formation with REE^{3+} ions [67].

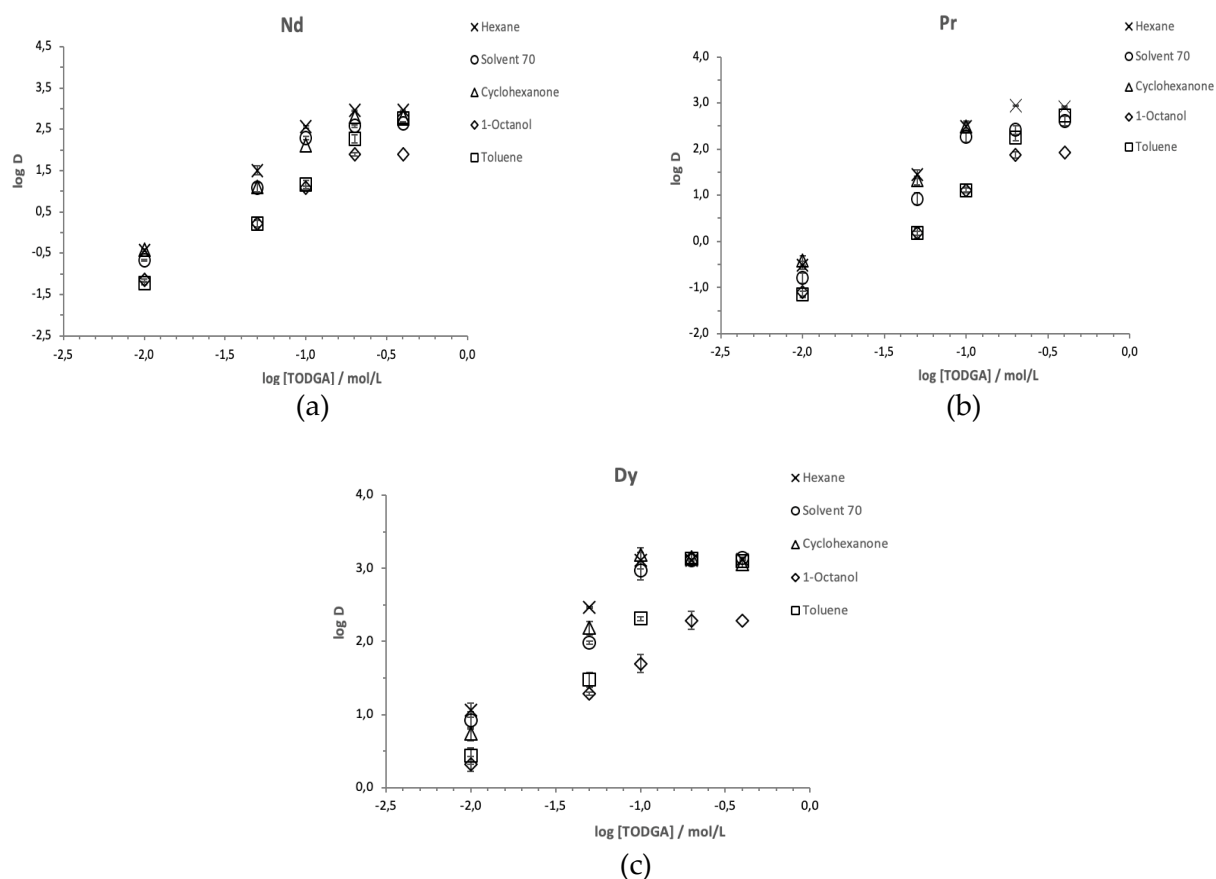


Figure 5.12. The dependence of the distribution ratios of (a) Nd, (b) Pr, and (c) Dy on TODGA concentration in Solvent 70, hexane, 1-octanol, cyclohexanone, and toluene from an aqueous phase that consisted of 4000 mgL^{-1} of the magnet leached in 3 mol/L HNO_3 . The organic-to-aqueous phase ratio was kept at 1:1 and the temperature was $25 \pm 1^\circ \text{C}$.

From a NdFeB recycling standpoint it was interesting to observe that the distribution ratios of other elements in the leachate reached values less than 0.1 (the highest measured for B and Al in cyclohexanone was around 0.5, which can be attributed to the ability of cyclohexanone to extract these ions out of the solution by itself [59]). The greatest advantage of TODGA in hydrometallurgical recycling of the NdFeB magnets is the low distribution ratios of Fe in TODGA. Fe comprises the majority of the material dissolved in nitric acid solutions. In a study by Zhu et al. [68], it was shown that divalent ions with ionic radii smaller than 80 pm and trivalent ions with ionic radii smaller than 70 pm exhibit low distribution ratios in extraction with TODGA in n-dodecane. The work performed in this research is in accordance with that study, showing that larger ions of REEs are prioritized in the extraction process.

It is important to determine separation factors when studying an extraction process, as these can help determine the number of stages needed for achieving high purity of the elements of interest. The focus here has been to determine the separation factors between HREEs (Dy in this case) and LREEs (Nd and Pr). Higher separation factors between the HREEs and LREEs are generally achieved at lower TODGA concentration due to higher affinity for extraction of larger HREE ions and limited availability of TODGA ligands. The highest separation factors for Dy were reached at 0.01 mol/L TODGA in Solvent 70, while REEs are extracted selectively and completely as a group at 0.1 mol/L TODGA in all diluents. Separation factor values can be found in [14].

Stripping was conducted with 0.01, 0.1 mol/L HNO₃, and MQ water [14]. The recovery of the REEs reached almost 100% in MQ water for Nd, Pr, and Dy, while 0.1 mol/L HNO₃ performed very poorly, with only 50% of metals stripped. Incomplete recovery was also achieved with 0.01 mol/L HNO₃. It was shown that only MQ water with no NO₃⁻ counter-ions was enough to break the complex from the organic phase and achieve high stripping efficiency, as can be concluded from Equation 3.16.

5.3.2. Extraction of REEs from the leachate obtained by sulfonation, selective roasting and water leaching using D2EHPA in various diluents

D2EHPA was used for extraction of REEs from a leachate obtained by sulfonation, selective roasting and water leaching that was provided to us in liquid form. More information about this particular type of selective leaching can be found in [48]. This investigation of extraction of REEs from SO₄²⁻ media is also interesting, since H₂SO₄ as such was shown to be an efficient leaching agent for non-roasted NdFeB waste (Section 5.1).

The leachate composition was determined using ICP-OES and the detected concentrations of Nd, Dy, Pr, Gd, Co and B in the leachate are shown in Table 5.3.

Table 5.3. Concentrations of the metals of interest in the leachate measured with ICP-OES. The measurement was performed with ICP-OES after diluting the obtained leachate with 0.5 M HNO₃

Element	Concentration / mM
Nd	9.1 ± 0.9
Dy	2.7 ± 0.6
Pr	3.2 ± 0.4
Gd	0.69 ± 0.16
Co	0.17 ± 0.09
B	0.55 ± 0.14
other	below detection limit

It was not possible to detect any Fe in the solution by ICP-OES, which shows that this leaching method is very selective [48]. The pH value of the solution was determined to be roughly 5.2. The concentration of sulfate ions was determined to be $[SO_4^{2-}] = 23 \pm 1$ mM and was kept constant throughout the series of experiments.

Solvent extraction experiments with 0.3, 0.6, 0.9 and 1.2 mol/L D2EHPA in Solvent 70, hexane, octane, toluene, cyclohexanone, 1-octanol and chloroform showed that the distribution ratios of the REEs increased with D2EHPA concentration in all of the diluents mentioned (Figure 5.13). Higher distribution ratios were observed for the HREEs (Dy and Gd) than for the LREEs (Nd and Pr) in all diluents. This is a trend that has also been observed previously in a study by Mohammadi et al. [58]. Distribution ratios were generally higher in the aliphatic diluents (hexane, octane, and Solvent 70), followed by toluene, and lowest in the polar diluents (cyclohexanone, 1-octanol, and chloroform). Co distribution ratios were calculated to be around zero, while the distribution ratios of B stayed very low in every extraction system investigated, with the exception of the experiments with cyclohexanone and 1-octanol where around 10% of the B present in the solution was extracted. This phenomenon is attributed to the presence of a carbonyl group in cyclohexanone and the hydroxyl group in 1-octanol, which could allow the diluent molecules to form complexes with B that are soluble in the organic phase. Since the B concentration in the leachate was very low, some of the extraction could also be attributed to the diffusion of B into the organic phase. It was observed that 100% of all the REEs were transferred to the organic phase at 0.9 and 1.2 mol/L D2EHPA in hexane and octane, while no Co or B was extracted. The slope analysis, despite to some extent being compromised by the too high concentration of elements in the solution, suggests 2-3 D2EHPA dimers are spent on complex formation of REEs, with the slope slightly decreasing with the increasing polarity of the diluents. These results are in accordance with relevant studies in the field [58]. As mentioned before, slope analysis is a suggestive method and XAFS measurement should be performed to further ascertain the structure.

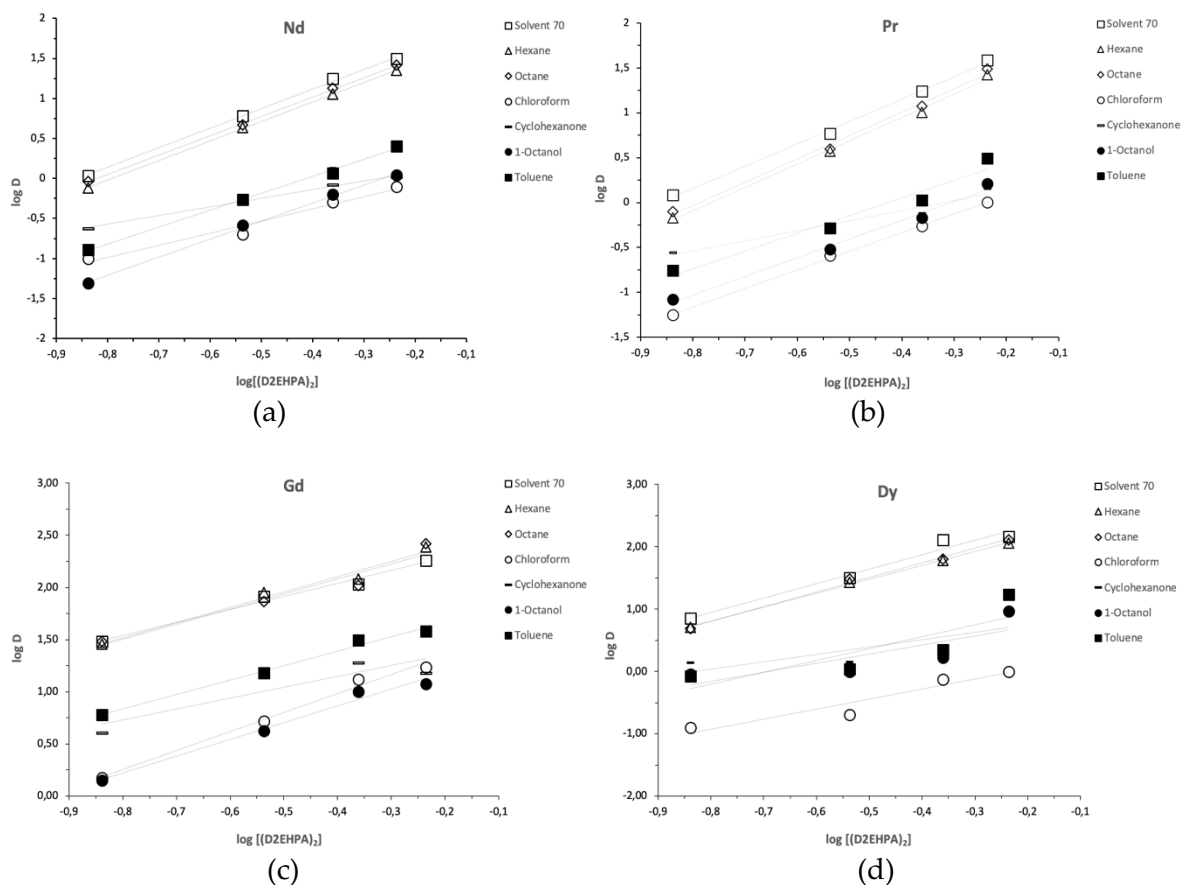


Figure 5.13. The influence of D2EHPA concentration on the extraction of (a) Nd, (b) Pr, (c) Gd, and (d) Dy from the aqueous phase consisting of 9.11 mmol/L Nd, 2.71 mmol/L Dy, 3.16 mmol/L Pr, 0.69 mmol/L Gd, 0.17 mmol/L Co, and 0.55 mmol/L B, with 0.3, 0.6, 0.9, and 1.2 mol/L D2EHPA, respectively, in Solvent 70, hexane, octane, toluene, cyclohexanone, chloroform, and 1-octanol. The temperature was kept at 25 ± 1 °C and $\Theta = 1$.

HREEs exhibited distribution ratios one order higher than those of LREEs, which corresponds to the decreasing ionic radii of these elements. The ionic radii of hydrolyzed Pr^{3+} , Nd^{3+} , Gd^{3+} , and Dy^{3+} are 0.99, 0.983, 0.938, and 0.912 Å, respectively [92]. The charge density will consequently increase as the ionic radius decreases, which contributes to the REE^{3+} binding to the D2EHPA molecule. This will favor the extraction of the HREEs over the LREEs. HSAB (hard soft acid base) theory divides the acids and bases into hard and soft [24], and can help predict the formation of salts and complexes. According to HSAB theory, Co^{2+} is a borderline acid, meaning it can act as a soft or hard acid depending on various factors, including removal of hydrate water, steric effects, etc. In this case, Co^{2+} acts as a soft acid that did not form a complex with the D2EHPA from the organic phase.

For a better comparison and understanding of the diluent effect on the extraction, the distribution ratios of Nd in 0.9 mol/L D2EHPA diluted in various diluents are presented in Figure 5.14. As in the case of the extraction with TODGA, the distribution ratios of Nd decrease with the polarity of the diluent in the following order: Solvent 70 > octane > hexane > toluene > cyclohexanone > 1-octanol > chloroform. The distribution ratios are one order higher in the aliphatic nonpolar diluents than in the aromatic and polar ones. D2EHPA is a

relatively nonpolar molecule, due to its 2-ethylhexyl chains. The high distribution ratios can be explained by good solubility of the D2EHPA extractant in the aliphatic nonpolar diluents, thus leading to less aggregation of the extractant molecules, resulting in higher distribution ratios for Nd. This does not apply however to cyclohexanone, in which distribution ratios for Nd are higher than in other polar diluents (1-octanol and chloroform) despite it having the largest dielectric constant (18.3). This extraction-enhancing phenomenon can be attributed to the oxygen donor atom in the cyclohexanone molecule, which could cause it to form complexes with the REE ions [93]. This phenomenon could also explain the extraction of B into the organic phase. Comparing the values of dielectric constants could have limitations, however, since the dielectric constant changes with the addition of the extractant and the altering concentration.

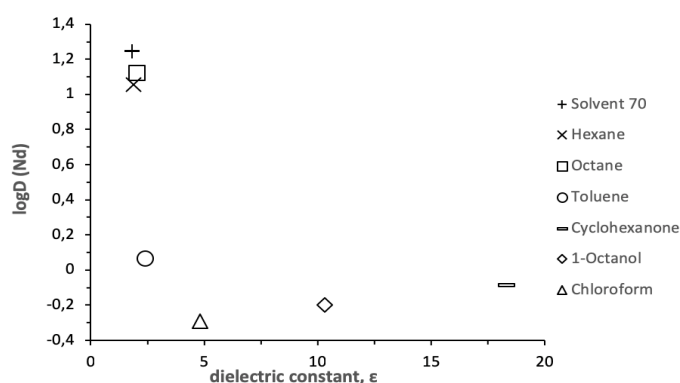


Figure 5.14. Distribution ratios of Nd (logarithmic value) plotted as a function of the dielectric constants of the diluents. The organic phase used was 0.9 mol/L D2EHPA diluted in Solvent 70, hexane, octane, toluene, cyclohexanone, chloroform, and 1-octanol. The aqueous phase consisted of 9.11 mmol/L Nd, 2.71 mmol/L Dy, 3.16 mmol/L Pr, 0.69 mmol/L Gd, 0.17 mmol/L Co, and 0.55 mmol/L B. The extraction conditions were 25 ± 1 °C and $\Theta = 1$

Since D2EHPA is an acidic extractant, the equilibrium pH in the aqueous solution will affect the extraction properties. In this case 0.3 mol/L D2EHPA in Solvent 70 was used as organic phase, while the equilibrium pH of the aqueous phase was altered. Increasing the pH values (Figure 5.15.) led to Dy and Gd extraction, followed by Nd and Pr. At pH = 1 light lanthanides (Nd and Pr) will be co-extracted with the heavy lanthanides with ratios of around 100%:50% (heavy:light). At around pH=1, no extraction of Co and B whatsoever could be observed. When the pH value was increased to 1.9, around 10% of B is extracted and around 20% of Co is extracted. Therefore, to avoid the co-extraction of the exogenes with the lanthanides, the equilibrium pH should be kept at or below a value of 1. Increasing the equilibrium pH to 2 will lead to complete extraction of the lanthanides in the solution into the organic phase, but with the disadvantage of the increased co-extraction of Co and B in minor quantities. This could lead to the need for more extraction stages, for example, in a mixer-settler set up.

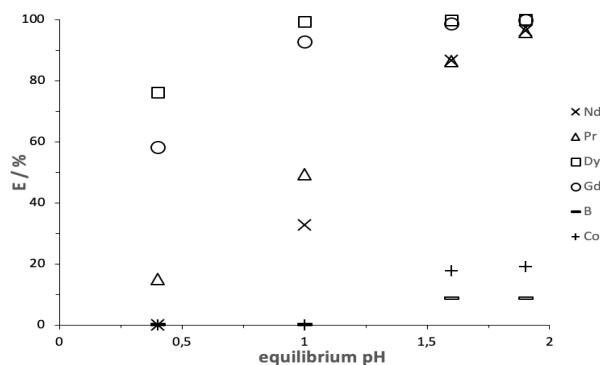


Figure 5.15. Percentages of extraction of Nd, Pr, Dy, Gd, Co, and B from the neodymium magnet leachate consisting of 9.11 mmol/L Nd, 2.71 mmol/L Dy, 3.16 mmol/L Pr, 0.69 mmol/L Gd, 0.17 mmol/L Co, and 0.55 mmol/L B with varied equilibrium pH values. The extraction conditions were 25 ± 1 °C and $\Theta = 1$. The organic phase used was 0.3 mol/L D2EHPA in solvent 70.

Separation of HREEs and LREEs can sometimes be important due to the difference in their price, different applications and purity requirements. In this research it was determined that the separation between the HREEs and the LREEs was highest when extracting with 0.3 mol/L D2EHPA in hexane, where almost the entirety of the Dy and Gd was extracted from the solution and around half of the amount (50%) of the LREEs present was extracted. It has also been demonstrated that at 0.9 mol/L and 1.2 mol/L D2EHPA concentrations in hexane and octane, the REEs are completely extracted out of the leachate solution as a group, leaving the exogenes (Co and B) within the solution. Separation factor values for all the extraction conditions can be found in [17].

Since D2EHPA is an acidic extractant, the stripping of extracted species from D2EHPA-based solvents is usually done by contacting the pregnant organic phase with an acid of a certain concentration. In this case the stripping studies were performed using the organic phases after extraction with 0.3 mol/L D2EHPA in hexane and 1.2 mol/L D2EHPA in octane. These were then brought into contact with aqueous solutions with various concentrations of HCl. It has been shown that the complete stripping of the elements, in principle REEs, back into an aqueous phase is achieved at 2 mol/L HCl or higher. More information about the stripping experiments can be found in [17].

5.3.3. Extraction of REEs from organic acids leachates using D2EHPA, TODGA, Cyanex 923, Cyanex 272 and TBP in various diluents

Since the organic acids were shown to be efficient in leaching of REEs from NdFeB waste, these leachates were tested in an array of extractants used today both in research and in industrial recovery of REEs.

Firstly, D2EHPA was used for recovery of REEs from citric and acetic acids leachate obtained under Section 5.2.2. The kinetics of the extraction were very fast. When contacting 1 mol/L D2EHPA in Solvent 70 with 1 M acetic acid and 1 M citric acid leachate, respectively, it took 1 minute to reach extraction equilibrium for all the elements (Figure 5.16 (a) and (b)). REEs are completely extracted from the leachate (>above 98%) in both cases, with the distribution ratios

being higher in the case of 1 mol/L acetic acid. For Dy 90% of the distribution ratios were not plotted as the ICP-OES was not sensitive enough to quantitatively determine the amount of remaining Dy in the aqueous phase after extraction. Fe was extracted from 1 M acetic acid leachate, while less than 50% of the Fe was extracted from the 1 mol/L citric acid leachate. This makes citric acid more attractive in terms of selective extraction of REEs from Fe. Both Co and B show low affinity for extraction with less than 10% of the total amount extracted into the organic phase, although distribution ratios of Co are one order higher in extraction from 1 M acetic acid. The selectivity of the extraction is a result of the equilibrium pH, which was around 3.5 after extraction from 1 mol/L acetic acid leachate, while it was around 2 after extraction from 1 mol/L citric acid. It has been previously shown [17] that increasing the equilibrium pH results in higher distribution ratios for REEs and Co when extraction is carried out using D2EHPA. Since the kinetics were very fast, all other bench-scale experiments were contacted for 1-3 minutes.

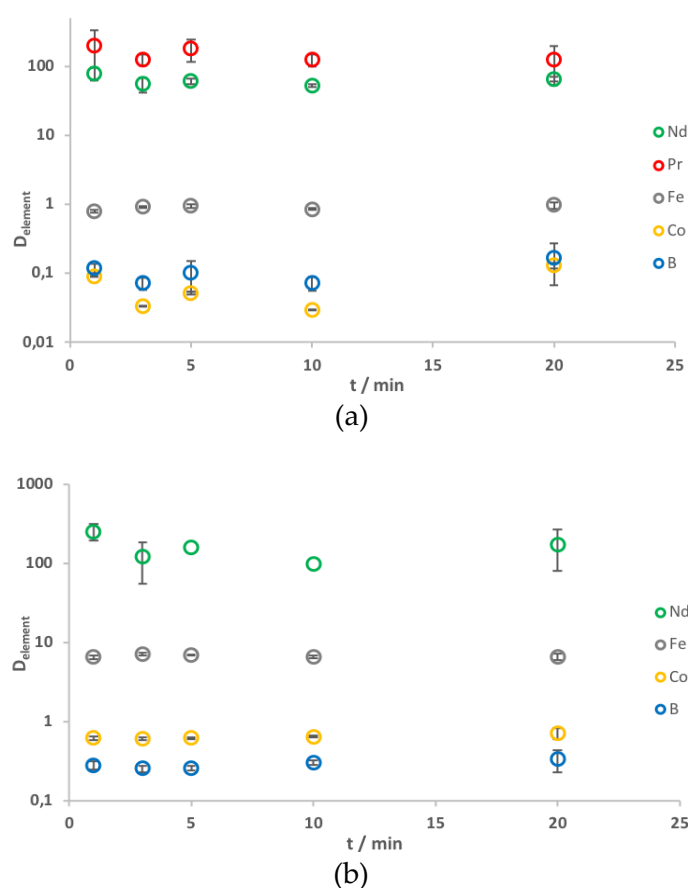


Figure 5.16. Extraction kinetics of Nd, Pr, Fe, Co and B using 1 mol/L D2EHPA in Solvent 70 from (a) 1 mol/L acetic acid and (b) 1 mol/L citric acid leachate solution, at $\Theta = 1$ and $t = 25 \pm 1$ °C with a shaking speed of 1500 rpm.

Extraction system temperature can have a significant effect on the overall extraction process and it is thus important to determine optimal thermodynamic conditions. The influence of temperature on the distribution ratios of Nd, Pr, Fe, Co and B in the system of extraction with D2EHPA from 1 mol/L acetic acid leachate and 1 mol/L citric acid leachate is shown in Figure 5.17 (a) and (b). The temperature gradient change did not have any significant effect on the distribution ratios of the elements from the leachates. All of the REEs were completely

extracted after 3 minutes contacting at 25 ± 1 °C, 45 ± 1 °C and 75 ± 1 °C. Fe extraction was also not affected by the temperature change, while a slight increase in Co extraction was observed in the case of 1 M acetic acid solution, however this was insignificant from a practical standpoint. All further experiments were therefore performed at 25 ± 1 °C.

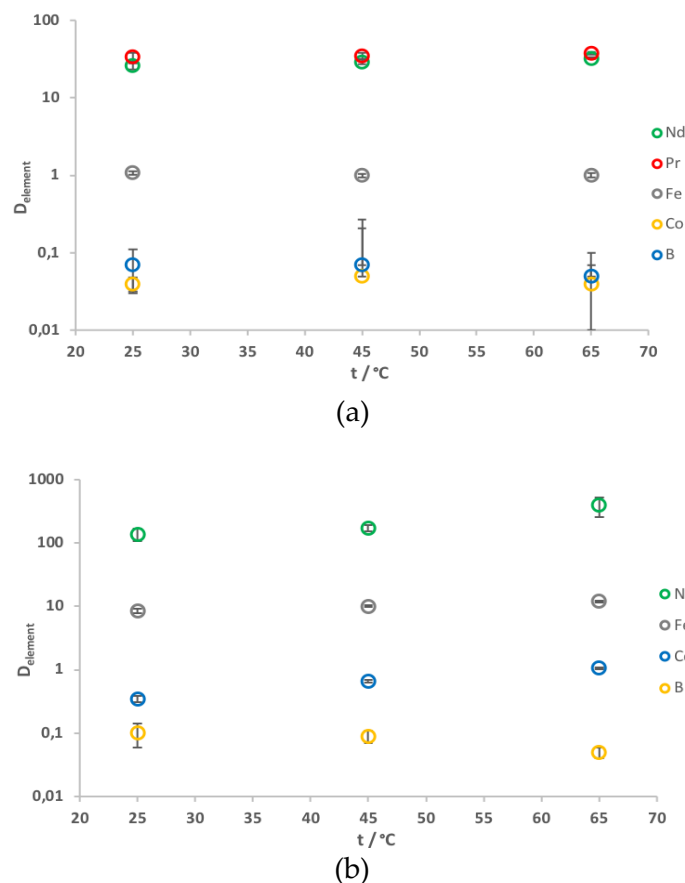


Figure 5.17. The effect of temperature on D for Nd, Fe, Co and B. The aqueous phase used was 1 M (a) citric acid and (b) acetic acid leachate, and the organic phase was 1 mol/L D2EHPA in Solvent 70. The O:A ratio was 1 and shaking speed was 1500 rpm.

D2EHPA dissolved in Solvent 70 in concentrations of 0.2, 0.4, 0.6, 0.8, and 1 mol/L was used as the organic phase for the extraction of the REEs out of the 1 M citric and 1 M acetic acid leachates to test the D2EHPA concentration effect on the extraction. Distribution ratios of two major elements composing the magnet, Nd and Fe, are presented in Figure 5.18. The distribution ratios of both REEs and Fe increased with increasing D2EHPA concentration in the organic phase, while the distribution ratios of Fe were one order of magnitude lower compared to Nd. The separation factors were calculated to determine the degree of separation [18] and it was determined that the highest was achieved at 0.2 mol/L D2EHPA extraction from 1 M acetic acid (161.9 ± 21.0). Separation factors between Nd and Fe were generally higher in the case of 1 mol/L acetic acid leachate but had reached a value of 129 ± 55 in extraction from 1 mol/L citric acid leachate, making these systems promising in separating valuable elements like Nd from large amounts of Fe usually present in NdFeB magnets. The fact that the D values were higher in the acetic acid case can be attributed to the equilibrium pH values. The pH was around 3.5 after the extraction from 1 mol/L acetic acid leachate and slowly increased with the decreasing D2EHPA concentration, but stayed

around 1.5 after the extraction from 1 mol/L citric acid leachate. As shown in another study [17], higher equilibrium pH values led to higher distribution ratios for REEs due to REE–D2EHPA complex formation, which is favored in higher equilibrium pH media. D2EHPA is an acidic extractant that exhibits the ion-exchange mechanism, with release of H^+ ions after the complex has been formed (Equation 3.12.). It was also shown that at the investigated conditions (0.2–1 mol/L D2EHPA in Solvent 70), less than 1% of both B and Co were extracted from the leachates, making this system even more feasible in terms of selective REEs recovery.

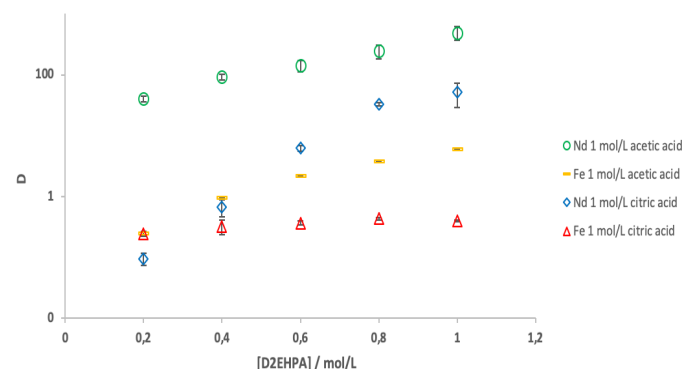


Figure 5.18. Distribution ratio of Nd and Fe as a function of the concentration of D2EHPA in a small-scale solvent extraction set-up ($V_{org}/V_{aq} = 1$; 10 min shaking at 1500 rpm on an adaptable vortex mixer). The aqueous phase was a leachate (citric and acetic acid 1 mol/L; S:L 1g /50 mL; 25 °C; 24 h; 400 rpm stirring) using D2EHPA in Solvent 70 solutions as extracting agents, while temperature was thermostatically kept at $25 \pm 1^\circ\text{C}$.

The preliminary solvent extraction test shown in Figure 5.19 shows that D2EHPA was the most suitable extractant for selective extraction of the REEs from glycolic and maleic acid leachates, while keeping other metals mostly in the aqueous phase. TODGA showed good results in extraction only from the maleic acid leachate. The other extracting agents used showed low distribution ratios for REEs, so that the separation factor between them and transition metals was poor and not sufficient for a feasible extraction step. These differences of extraction efficiency can be explained by the fact that the extractants tested had different mechanisms of extraction, for instance D2EHPA is an acidic extractant, whereas TBP, TODGA and Cyanex 923 are solvating extractants. This means that, according to equation 3.16, solvating extractants require anions present in the aqueous phase to form complexes with the extractant molecules and metallic cations. Thus, a change in the leachates means a change of the counter-ions in the solution, meaning the extraction mechanism will be compromised. This was noticed with TODGA in the glycolic acid leachate. It seems, however, that extraction of REEs using TODGA was not hindered in the maleic acid leachate. For acidic extractants, equation 3.12 shows that cations are directly exchanged with the hydrogen atoms of the extractants, regardless of the counter-ions. Some color changes were observed during the experiments. At first the aqueous phase was yellow, and this remained the same for some experiments (for instance with TODGA), whereas in other experiments, such as Cyanex 923 with maleic leachate, the inverse was seen and the organic phase became yellow. For D2EHPA, both phases became transparent. In the case of Cyanex 923 with glycolic leachate, a third phase was observed, appearing to be an emulsion and insoluble in both aqueous and organic media. This

phenomenon can also appear during industrial processes, such as the PUREX process, and should be avoided. [94] From the results obtained, the following optimization tests were performed using D2EHPA as an extractant.

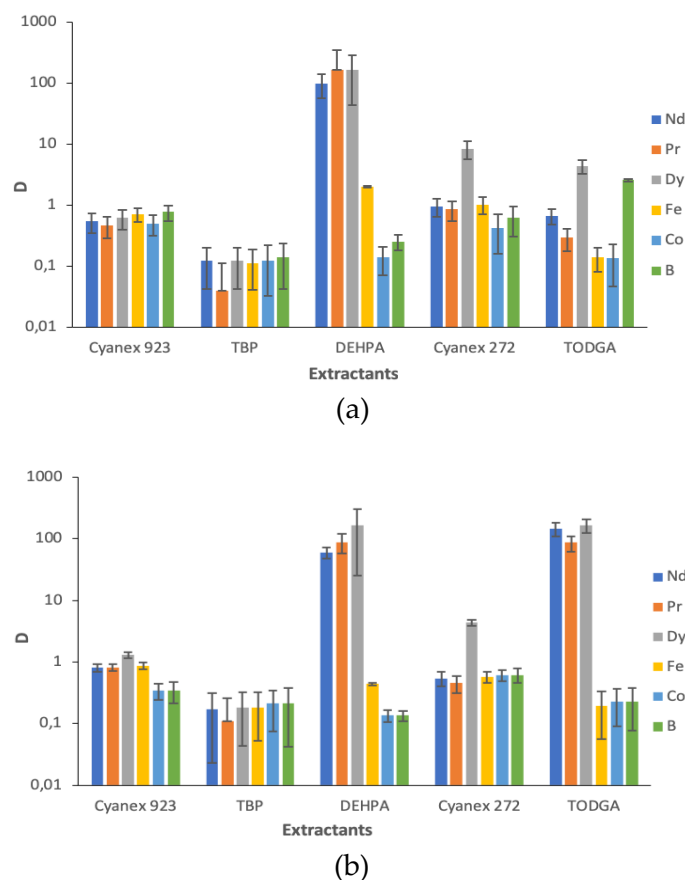


Figure 5.19. Distribution ratios for Nd, Pr, Dy, Fe, Co and B in 1 mol/L solutions of different extractants (Cyanex 272, 923, TBP, D2EHPA and TODGA) in Solvent 70. The aqueous phase was 1 mol/L a) glycolic and b) maleic acid, the organic to aqueous phase ratio was 1:1 and the temperature was 25 ± 1 °C.

Solutions of D2EHPA in Solvent 70 were prepared, at 0.2, 0.4, 0.6, 0.8 and 1 mol/L, and extraction was performed from 1 mol/L glycolic and maleic acid leachates. The distribution ratios increased with increasing D2EHPA concentration, as there are more extractant molecules available to reach and solvate metal ions (Figure 5.20). 1 mol/L D2EHPA proved to be the most efficient of the 5 concentrations tested. Distribution ratios of Nd and Dy rise in a linear fashion, whereas for Pr there are more variations. The variation might be attributed to measurement errors, since Pr is present in low concentrations. D values of transition metals also increased with the rise in ligand concentration, however the D values are one order lower and significant separation between REEs and other elements is achieved. For the diluent effect tests, the 1 mol/L concentration was chosen.

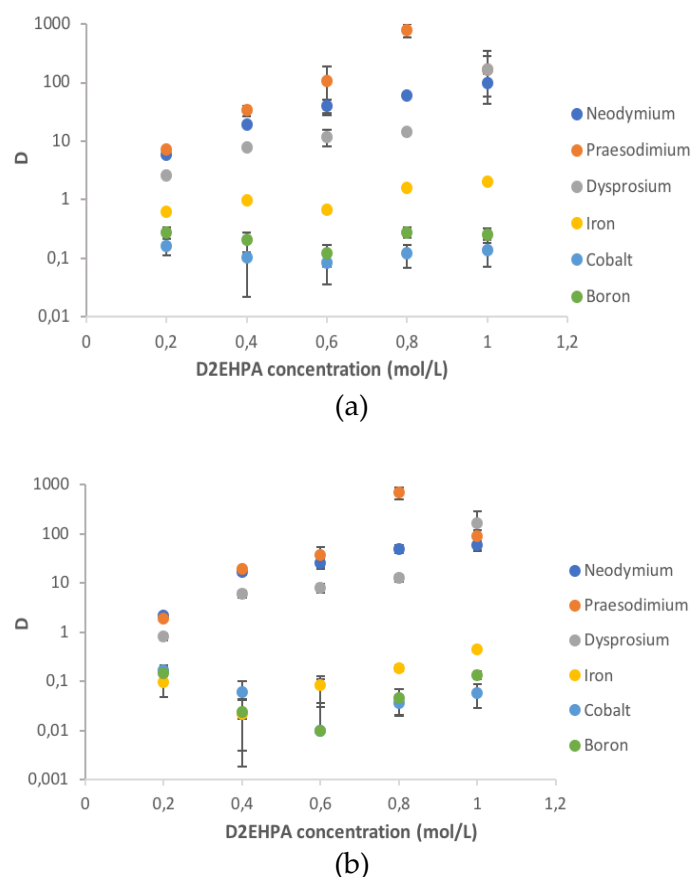


Figure 5.20. The dependence of distribution ratios of Nd, Pr, Dy, Fe, Co and B after extraction in solutions of D2EHPA in Solvent 70, at different concentrations (0.2, 0.4, 0.6, 0.8, and 1 mol/L). The aqueous phase was (a) 1 mol/L glycolic and (b) 1 mol/L maleic acid. $\Theta = 1$ and temperature was $25 \text{ }^{\circ}\text{C} \pm 1 \text{ }^{\circ}\text{C}$.

Lastly, the influence of the diluent used for the organic phase was tested (Figure 5.21.), as differences between the chemical and physical properties of the diluent can affect the extraction mechanisms. It is mostly the polarity and the ability to form hydrogen bonds and covalent bonds that matters when choosing a diluent. Previous studies have shown that nonpolar diluents, such as Solvent 70, are the best for an extraction process using hydrophobic extractants, such as TODGA with its long alkyl chains. [14] Experimental results showed that D2EHPA extraction efficiency decreases in the pentane > hexane > Solvent 70 > dodecane sequence. Octanol and cyclohexanone were deemed unsuitable as diluents as they extracted larger amounts of cobalt and boron and lower amounts of REEs than nonpolar solvents. Hexane-containing solvent, especially for tests with the maleic leachate, showed no extraction of either Co or B, and very low extraction of Fe, which is very interesting from the selectivity standpoint. Pentane also showed high efficiency, which could be because the pentane molecules are structurally more similar in terms of alkyl-chain length to D2EHPA alkyl-chains than to big aliphatic alkanes, such as dodecane and Solvent 70. Also, the dielectric constants of these diluents follow the trend of the results, as pentane is the most effective and has the lowest dielectric constant after Solvent 70. The fact that octanol and cyclohexanone diluents tend to allow more transition metal extraction can be explained, as they can participate themselves in an extraction mechanism using the oxygen atoms and bind to the metal ions.

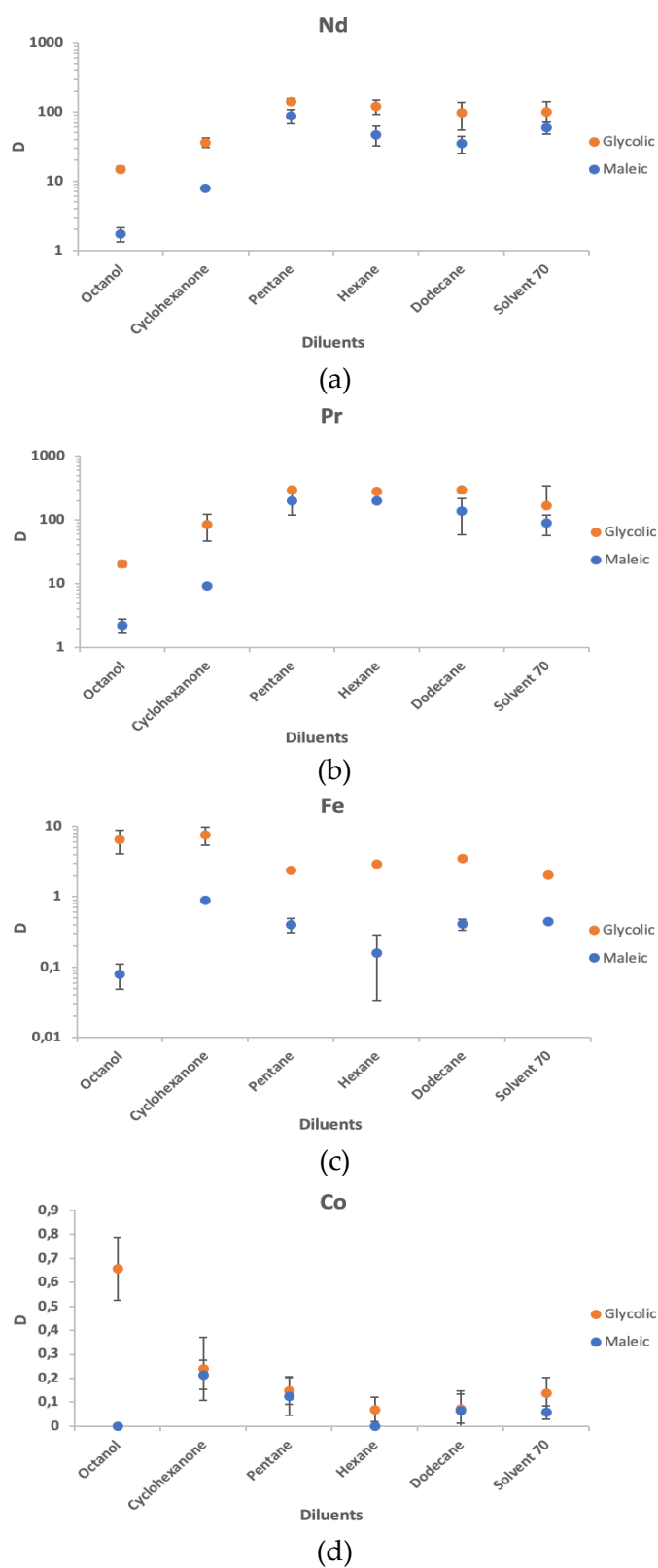
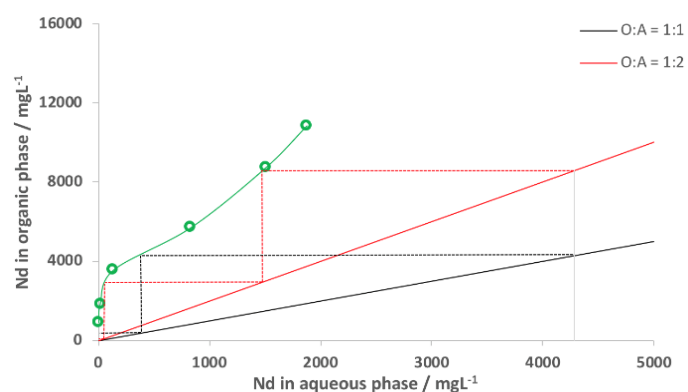


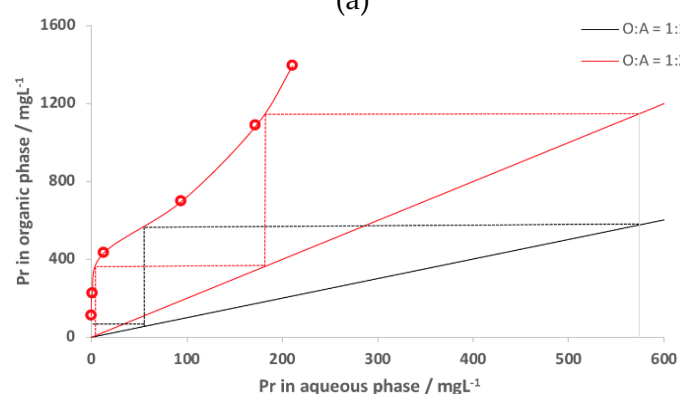
Figure 5.21. The dependence on distribution ratios of Nd, Pr, Fe and Co in 1 M solutions of D2EHPA in different diluents (1-octanol, cyclohexanone, pentane, hexane, dodecane and Solvent 70). The aqueous phase was 1 M glycolic or maleic acid, the organic to aqueous phase ratio was 1:1 and the temperature was 25 ± 1 °C.

5.4. Laboratory pilot scale recovery of REEs from neodymium magnet leachates

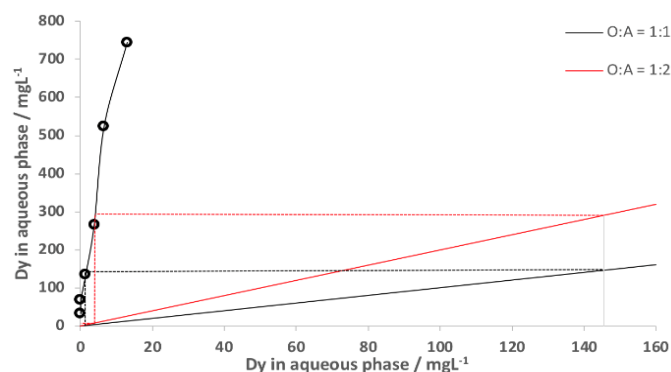
McCabe-Thiele diagrams for extraction from 1 mol/L citric acid using 1 mol/L D2EHPA in Solvent 70 are shown in Figure 5.22 and were constructed in order to determine the number of ideal stages for the extraction of REEs out of the 1 mol/L citric acid leachate. The extraction parameters used were the ones from previous results in kinetics and temperature experiments, while the O:A ratios used were 1:6, 1:4, 1:2, 1:1, 2:1 and 4:1. The isotherms shown in Figure 5.22 a), b) and c) show the concentration of Nd, Pr and Dy, respectively, at various O:A ratios. The vertical lines show the concentration of the REE in the aqueous feed (leachate), 4280 ± 25 mg/L Nd, 574.5 ± 2.1 Pr and 145.4 ± 0.3 Dy at the intersection with the x-axis. The dashed lines show the number of theoretical stages for complete extraction of the REEs at O:A ratio 1:1 (black) and 1:2 (red). For the O:A ratio 1:1 the number of ideal stages was determined to be 2, while for the 1:2 ratio it was determined that the number of ideal stages needed to extract Nd and Pr was 3 (although the majority of Nd and Pr is extracted in the first two stages), and 2 for Dy. To decrease the organic/aqueous ratio and achieve a more concentrated loaded organic phase a 1:2 ratio was chosen and 3 stages were used for complete extraction of REEs.



(a)



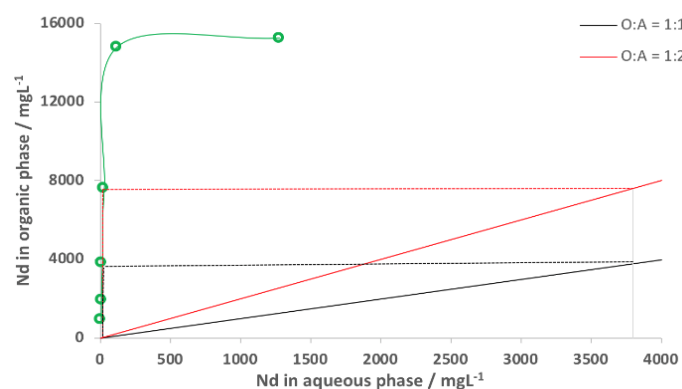
(b)



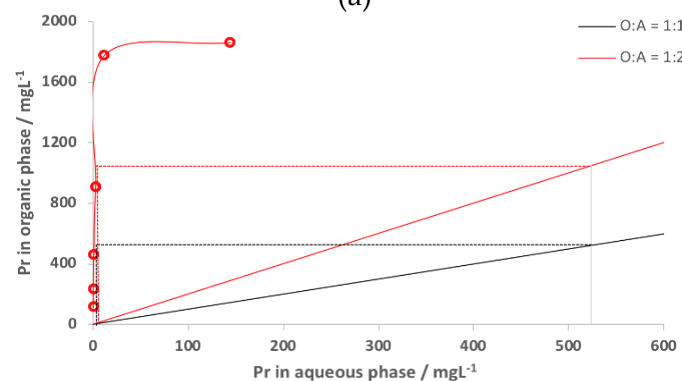
(c)

Figure 5.22. McCabe-Thiele diagrams with theoretical extraction steps for the solvent extraction of (a) Nd, (b) Pr, and (c) Dy using 1 mol/L D2EHPA in Solvent 70 from the 1 mol/L citric acid leachate. The contact time was 3 min., temperature was kept at 25 ± 1 °C, shaking speed was 1500 rpm and O:A ratios were 1:6, 1:4, 1:2, 1:1, 2:1 and 4:1.

Similar to the case for the 1 mol/L citric acid, the McCabe-Thiele diagrams were constructed for the extraction with 1 mol/L D2EHPA in Solvent 70 from 1 mol/L acetic acid leachate (Figure 5.23). The isotherms were plotted for data for 5 different O:A ratios 1:6, 1:4, 1:2, 1:1, 2:1 and 4:1, while the extraction conditions were the ones previously determined in the kinetics and temperature study. It was determined (dashed lines on the graphs), that the majority of the REEs are extracted after one stage for both 1:2 and 1:1 O:A ratios, but to ensure complete extraction of the REEs from the leachate 2 stages of extraction were chosen for the 1 mol/L acetic acid case.



(a)



(b)

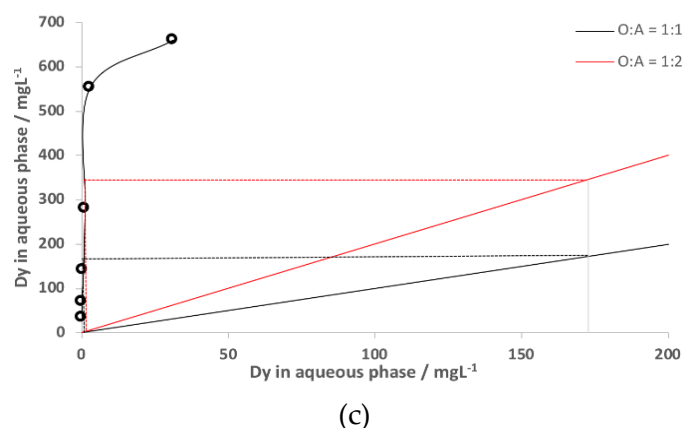
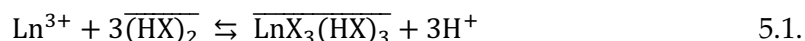


Figure 5.23. McCabe-Thiele diagrams with theoretical extraction steps for the solvent extraction of (a) Nd, (b) Pr, and (c) Dy using 1 mol/L D2EHPA in Solvent 70 from the 1 mol/L acetic acid leachate. The contact time was 3 min., temperature was kept at 25 ± 1 °C, shaking speed was 1500 rpm and O:A ratios were 1:6, 1:4, 1:2, 1:1, 2:1 and 4:1.

The stripping of the REEs and other elements from the loaded organic phase in the 1 mol/L citric acid case was tested using 4 different acids (2 mol/L HNO_3 , 2 mol/L HCl , 3 mol/L citric acid and 4 mol/L acetic acid). The inorganic acids were chosen based on previous studies of the stripping process [17, 44, 83], while organic acids were the most concentrated ones that were feasible to prepare on a laboratory scale. Since the process is based on extraction from organic acids leachates, the same organic acids were used to test the feasibility for stripping of REEs from the loaded organic phase, in order to have the whole process run with organic acids. It was, however, not feasible to completely strip back the REEs using 3 mol/L citric acid or 4 mol/L acetic acid at any of the O:A ratios tested. This is because D2EHPA needs stronger acids to strip back the elements after the extraction. The results for 2 mol/L HNO_3 and 2 mol/L HCl as stripping agents were much better. Both were able to back-extract Nd and Pr almost completely at every A:O ratio after 1-minute contact time. Dysprosium showed to be challenging to strip, since the A:O ratio needs to be over 1:1 to strip 80% of the Dy with 2 mol/L HNO_3 and a mere 60% in 2 mol/L HCl . Since significantly less Fe is stripped when using HNO_3 than when using HCl , 2 mol/L HNO_3 was used for stripping to achieve an REE-rich strip. Two stages were enough for complete stripping of Nd, Pr and Dy to potentially avoid more Fe stripping. Similar stripping experiments were carried out using 1 mol/L acetic acid extraction. The solutions 3 mol/L citric and 4 mol/L acetic acid were not ideal for stripping since an A:O ratio above 4:1 would be needed for less than 80% stripping of Nd and Pr, and a mere 20% of Dy was stripped even at a 6:1 ratio. For the same reason as for the 1 mol/L citric acid case, 2 mol/L HNO_3 was chosen, since almost no Fe is back-extracted and 90% of Nd and Pr are stripped and 60% of Dy. Two stages were chosen.

It can be observed that around 93% of Nd and Pr, and 98% of Dy were extracted after 2 mixer-settler stages using O:A ratio 1:2 (Figure 5.24.). Adding one extra extraction stage leads to complete extraction (around 100%) of all the REEs, but it also leads to higher extraction of Fe into the organic phase (around 50% after 2 stages and around 70% after 3 stages). Less than 10% of B and 20% of Co were extracted into the organic phase during 3 stages of extraction, so B and Co are expected to be minor impurities in the back-extraction product. According to the equilibrium pH, the pH decreased during extraction. This is in accordance with equation 1,

which shows the usual extraction reaction of lanthanides using acidic extractants like D2EHPA[95]:



, where Ln represents the lanthanide ion and HX represents D2EHPA.

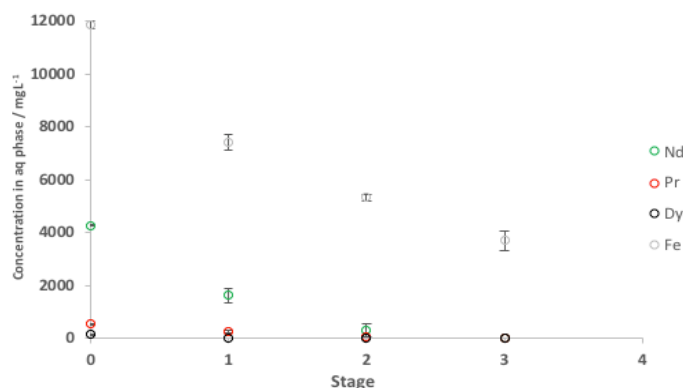


Figure 5.24. Aqueous phase concentration of Nd, Pr, Dy and Fe of mixer-settler stages in the REE extractions. The aqueous phase used was the 1 mol/L citric acid leachate, and the organic phase was 1 mol/L D2EHPA in Solvent 70. The O:A ratio was 1:2, number of stages $n=3$, and flows of organic and aqueous phase 4 mL/min. Equilibrium pH values of the aqueous phases in the extraction steps from 1 to 3 were ≈ 2.4 , ≈ 2.2 and ≈ 2.1 , respectively.

After the extraction the organic phase was pumped into the stripping part of the mixer-settler. For stripping 2 mol/L HNO_3 was used and an A:O ratio of 1:1. It can be observed in Figure 5.25 that after 1 stage very little of the REEs are back-extracted into the stripping solution. However, after 2 stages, around 92% of Nd was back-extracted into the stripping solution, while Pr was quantitatively back-extracted. A little bit less than 60% of Dy was recovered this way. In the two stages of stripping, around 3% of the initial Fe concentration in the leachate was back-extracted into the stripping solution. Less than 5% of B and Co were also stripped, which makes this process selective for the recovery of REEs, see Table 5.4. To increase the recovery of Dy and to quantitatively extract Nd, one more stripping stage could be added to the stripping, but that would lead to higher Fe co-stripping, which could compromise the process in terms of Fe selectivity.

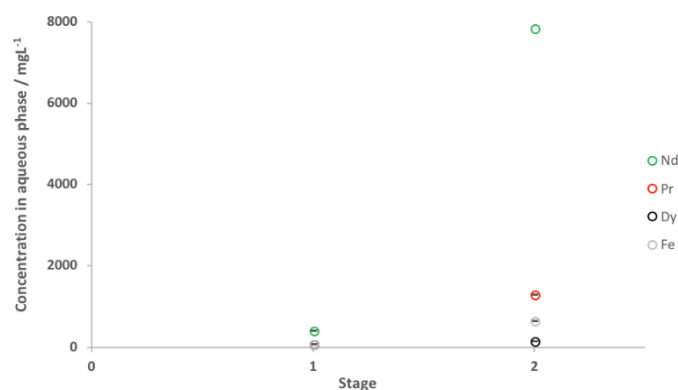


Figure 5.25. Aqueous phase concentration of Nd, Pr, Dy and Fe of mixer-settler stages in the REE stripping products. The aqueous phase (stripping agent) used was 2 mol/L HNO_3 , and the organic phase was the loaded organic phase after extraction from 1 mol/L citric acid (O:A = 1:2, 3 stages). The O:A ratio was 1:1, number of stages $n=2$, and flows of organic and aqueous phase 4 mL/min.

Table 5.4. The concentration of elements in citric acid leachate after 3 extraction stages with 1 mol/L D2EHPA in Solvent 70 and concentration of the elements in the stripping product after 2 stripping stages of the mixer-settler 1 mol/L citric acid process using 2 mol/L nitric acid

Element	Leachate/ mgL^{-1}	Raffinate/ mgL^{-1}	Stripping product / mgL^{-1}
Nd	4280 ± 25	13.31 ± 4.26	≈ 7859
Pr	574.5 ± 2.1	-	1252 ± 13
Dy	145.4 ± 0.3	-	163.5 ± 1.4
Fe	11879 ± 143	3699 ± 362	632.5 ± 7.6
Co	247.5 ± 2.5	217.7 ± 5.3	24.01 ± 0.28
B	177.1 ± 2.4	137.7 ± 6.6	15.15 ± 0.33

The concentrations of the REEs and Fe in the aqueous feed in each stage of the extraction process using 1 mol/L D2EHPA and 1 mol/L acetic acid leachate are presented in Figure 5.26. More than 99% of Nd, Pr and Dy were extracted in 2 stages, while 90% of Fe was also extracted, which is significantly more than in the case of the 1 mol/L citric acid leachate and can be a limiting factor. Around 40% of the Co and B were extracted into the organic phase. As in the case of 1 mol/L citric acid, the equilibrium pH decreased during extraction, which is also in accordance with equation 1. The extraction results for both 1 mol/L citric acid and 1 mol/L acetic acid agreed well with the results from McCabe-Thiele construction experiments when predicting the number of stages needed for complete extraction of REEs from the extraction systems used in the experiments.

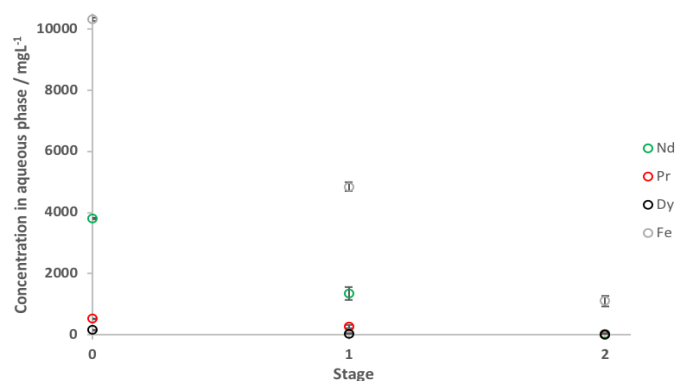


Figure 5.26. Aqueous phase concentration of Nd, Pr, Dy and Fe of mixer-settler stages in the REE extractions. The aqueous phase used was the 1 mol/L acetic acid leachate, and the organic phase was 1 mol/L D2EHPA in Solvent 70. The O:A ratio was 1:2, number of stages $n=2$, and flows of organic and aqueous phase 4 mL/min. Equilibrium pH values for stages 1 and 2 were ≈ 3.9 and ≈ 3.2 , respectively.

After 2 stages of extraction using 1 mol/L D2EHPA in Solvent 70, the loaded organic phase was pumped forward to the stripping part, where 2 mol/L HNO_3 was used as the stripping agent in 2 stages of back-extraction. After those 2 stages more than 92% of Nd, 100% of Pr and 50% of Dy (according to Table 5.5) from the original leachate were recovered back into the stripping solution. As for the Fe back-stripping, around 8% of Fe from the original leachate was co-stripped into the stripping solution, which is more than in the case of 1 mol/L citric acid, and even greater in absolute numbers (1000 ppm higher concentration in the strip). Co was back-extracted at 30% of the initial leachate value, and less than 5% of B was back-extracted, which is a much higher value for Co, pointing to the fact that a 1 mol/L citric acid process is much more selective from the REE-impurities point of view.

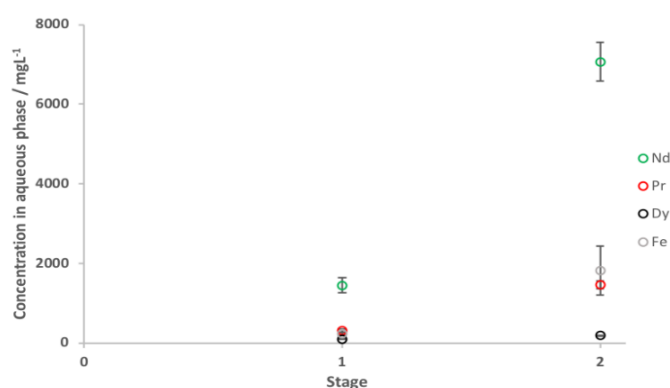


Figure 5.27. Aqueous phase concentration of Nd, Pr, Dy and Fe of mixer-settler stages in the stripping of the REEs. The aqueous phase (stripping agent) used was 2 mol/L HNO_3 , and the organic phase was the loaded organic phase after extraction from 1 mol/L acetic acid based leachate (O:A = 1:2, 2 stages). The O:A ratio was 1:1, number of stages $n=2$, and flows of organic and aqueous phase 4 mL/min.

Table 5.5. The concentration of elements in acetic acid leachate, the aqueous phase after 2 extraction stages with 1 mol/L D2EHPA in Solvent 70, and concentration of the elements in the stripping product after 2 stripping stages of the mixer-settler 1 mol/L acetic acid process using 2 mol/L nitric acid.

Element	Leachate/ mgL ⁻¹	Raffinate/ mgL ⁻¹	Stripping product / mgL ⁻¹
Nd	3803 ± 25	25.15 ± 30.13	6961 ± 74
Pr	523.5 ± 6.1	2.90 ± 5.03	1448 ± 22
Dy	172.8 ± 0.4	0.84 ± 0.76	181.4 ± 2.4
Fe	10317 ± 48	1103 ± 179	1639 ± 14
Co	258.6 ± 1.6	149.7 ± 20.6	190.7 ± 0.5
B	198.0 ± 2.3	131.2 ± 2.1	18.89 ± 0.19

6. CONCLUSIONS

The goal of the work presented in this thesis was to find feasible, environmentally friendly methods for recovery of REEs from neodymium magnet waste. This was done by leaching of the waste using organic and inorganic acids followed by solvent extraction using both traditionally used organophosphorus compounds as well as TODGA.

Two types of neodymium magnet wastes used were the HD NdFeB powder and its roasted form, the roasted NdFeB powder. They were characterized by determination of total element concentrations after dissolution in *aqua regia* as well as using techniques like SEM/EDX and XRD. Both powders contained over 25 % of REEs which makes them a feasible secondary source of REEs, containing mainly Nd with some small percentages of Dy and Pr. SEM analysis of the neodymium magnet powder before and after roasting showed significant changes in the morphology of the powder. EDX analysis showed that the original powder was composed of a NdFeB matrix and further confirmed the redistribution of the elemental composition that ensued during roasting. XRD analysis showed the HD NdFeB powder was composed mainly of $\text{Nd}_2\text{Fe}_{14}\text{BH}_3$, a hydride formed during the hydrogen decrepitation process while the roasted powder showed high amounts of Nd_2O_3 and Fe_2O_3 .

The inorganic acids HNO_3 , HCl , H_2SO_4 and $\text{CH}_3\text{SO}_3\text{H}$ were able to leach over 90 % of the REEs from HD NdFeB powder at 1 mol/L concentration, 1/50 g/mL and temperature of $25 \pm 1^\circ\text{C}$. Fe and Co showed similar leaching properties while the process was selective towards Ni. Since organic acids like acetic and citric acid exhibited slow kinetics at leaching of HD NdFeB magnet the powder was roasted to achieve oxides that are easier to dissolve. Acetic, citric, maleic and glycolic acid showed good leaching properties for REEs, Fe, and Co. Of all the concentrations studied, 1 mol/L citric, acetic, glycolic and maleic acid exhibited the best leaching properties. Over 90% of REEs were leached during 24 h with a concentration of 1 mol/l of all the mentioned acids. Co-leaching of Fe and Co into the solution could not be avoided due to similar dissolution properties as for the REEs. Changing the S:L ratio from 1/30 to 1/80 g/mL in 1 mol/L citric acid showed no difference in leaching efficiency during the 24 h leaching time, while 1 mol/L acetic acid after 24 h showed significantly less Fe leached with a S:L ratio 1/30 g/mL comparing to other S/L ratios investigated. In the case of 1 mol/L glycolic and maleic acid decreasing the S/L ratio enhanced the leaching efficiency for all metals tested, giving results comparable to those where mineral acids were used.

TODGA was used for extraction from the leachate obtained by dissolution of HD NdFeB powder in HNO_3 . The concentration over 2 M HNO_3 was needed for achieving highest distribution ratios for REEs. The distribution ratios increased with the increasing TODGA concentration. TODGA was shown to be very selective towards REEs that were extracted in much higher quantities than other impurities. Various diluents were tested and it was determined that the extraction efficiency for REEs decreased in the following order hexane > cyclohexanone > solvent 70 > toluene > 1-octanol. Highest separation factors between Dy and other REEs (Nd and Pr) were observed at 0.01 mol/L TODGA in Solvent 70, while REEs were completely extracted using 0.1 mol/L TODGA in hexane, Solvent 70 and cyclohexanone. Around 3 TODGA molecules were needed for complex formation according to slope analysis. Stripping was efficient using MQ water.

D2EHPA was used for extraction of REEs from a sulfate-based leachate. The distribution ratios increased with the increasing D2EHPA concentration with heavy REEs exhibiting one order higher distribution ratios than the light ones. Various diluents were used and it was shown that the extraction efficiency decreases in the following order aliphatic diluents (hexane, octane, Solvent 70) > toluene > polar diluents (cyclohexanone, 1-octanol, chloroform). At 0.9 and 1.2 mol/L D2EHPA the REEs are extracted as a group in hexane and octane while the best separation between the heavy and the light were found at 0.3 mol/L D2EHPA in hexane. The stripping was efficient using 2 mol/L HCl.

Extraction was tested on the glycolic and maleic leachates and different organic phase compositions. Low distribution ratios and poor separation factors between REEs and other metals were determined for TBP, Cyanex 272 and 923, using Solvent 70 as a diluent. However, for TODGA in Solvent 70 with the maleic leachate, and for D2EHPA Solvent 70 with both leachates, D values showed that REEs were extracted preferentially from the aqueous phase, contrary to Fe, Co and B. This shows that these types of leachate have potential future use on a large scale in terms of selectively extracting REEs from other impurities. Non-polar aliphatic diluents, such as pentane and hexane, showed the best efficiency.

Preliminary solvent extraction tests with 1 mol/L D2EHPA in Solvent 70 on the leachates in 1 mol/L citric and acetic acid, the REEs distribution ratios increased with increasing D2EHPA concentration from 0.2 mol/L to 1 mol/L. Higher distribution ratios were achieved in acetic acid with higher SF between Nd and Fe, but good separation between Nd and Fe was also achieved in extraction from 1 M citric acid leachate. The study showed significant results with respect to organic acids leaching and further extraction of REEs from the leachate using D2EHPA.

A pilot scale process was developed using 1 mol/L D2EHPA in Solvent 70 as an organic phase use in extraction of the 1 mol/L citric and acetic acid based magnet leachates. A McCabe-Thiele diagram was constructed, resulting in the indication that 3 stages would be necessary for systems containing 1 M citric acid, while 2 stages were necessary for leachates based on 1 M acetic acid. Both systems performed excellently in extracting the REEs out of the leachate, while the 1 M citric acid aqueous-1M D2EHPA system was much more selective towards iron extraction than 1 M acetic acid aqueous-1M D2EHPA system. 2 M HNO₃ stripping agent was used over 2 M HCl due to less Fe stripping. The solutions of 3 M citric acid and 4 M acetic acid did not turn out to be good enough stripping agents to make this process completely organic acids-based. During stripping in 2 stages with A:O = 1:1 around 92% of Nd was back-extracted into the stripping solution. Pr was quantitatively back-extracted and 60% of Dy was stripped from the process using 1 M citric acid leachate. Around 3% of the Fe was stripped back, which makes this process excellent for the Fe removal from these waste streams. In the process using 1 M acetic acid over 99% of Nd, Pr and Dy were back extracted in 2 stages, while 90% of Fe was extracted to a far greater extent than in the case of the 1 M citric acid process. After stripping using 2 M HNO₃ 92% of Nd, 100% of Pr and 50% of Dy had been recovered, as well as 8% Fe, which is 1000 ppm more than in the case of 1 M citric acid.

7. FUTURE WORK

Additional work could be performed on optimizing the processes developed in this thesis. Some of the aspects that could be further worked on are listed below.

1. The selectivity towards REEs in the leaching step should be improved, especially considering the presence of high amounts of Fe and other impurities in the neodymium magnet waste.
2. Clarification of the structure of the complexes and speciation of the metal species that exist in the leachates (especially leachates of organic acids) and the effect their chemical conformation has on the solvent extraction process. This is also coupled to similar studies of the structures of the complexes formed in the organic phase both in extraction from inorganic and organic acids aqueous media.
3. Investigation of possible actions to minimize the amounts of secondary waste formed during the leaching and solvent extraction processes.
4. Using organic acids as stripping agents in order to make the whole extraction process based solely on organic acids as aqueous phases.
5. Some other extractants based on the CHON principle could be further studied.

8. ACKNOWLEDGEMENTS

The work presented in this thesis was funded from the European Community's Seventh Framework Programme ([FP7/2007–2013]) under grant number No. 607411 (MC-ITN EREAN: European Rare Earth Magnet Recycling Network). ENVIREE project (Environmentally friendly and efficient methods for extraction of rare-earth elements (REE) from secondary sources-ERA-MIN project 2015–2017) is acknowledged for contribution with additional funding.

I would like to thank my supervisors Teodora Retegan and Britt-Marie Steenari as well as my examiner Christian Ekberg for the support and scientific contribution to this work.

Special thanks go to Fredrik and to all my colleagues and friends at the Nuclear Chemistry and Industrial Materials Recycling Department who have stood there beside me on this path, helped with my work and made this journey a pleasant one.

My friends back home and the ones who are located around the world, thank you for the support, fun times and laughter.

Lastly, I would like to thank my mom and family who have always been a great support in all the challenges that I have faced in life.

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ABBREVIATIONS AND TERMS

$\alpha_{A/B}$	Separation factors between solutes A and B
θ	Ratio between the aqueous and organic phase
CHON	Consisting of carbon, hydrogen, oxygen and nitrogen
Cyanex 272	Di(2,4,4-trimethylpentyl) phosphinic acid
Cyanex 923	Mixture of trialkyl-phosphine oxides
D	Distribution ratio
D2EHPA	Di(2-ethylhexyl) phosphoric acid
E	Fraction extracted
EU	European Union
HD	Hydrogen decrepitated
HDDs	Hard disk drives
HEHEHP(PC88A)	2-ethylhexyl 2-ethylhexyphosphonic acid
HREEs	Heavy rare-earth elements
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectrometry
K_a	Acid dissociation constant
LREEs	Light rare-earth elements
NdFeB	Neodymium magnets
NiMH	Nickel metal hydride
O:A	Organic to aqueous phase ratio
pH_{eq}	Equilibrium pH
pK_a	$-\log_{10}(K_a)$
REEs	Rare-earth elements
S:L	Solid-to-liquid ratio
SEM/EDX	Scanning Electron Microscopy / Energy Dispersive X-ray Spectroscopy
SmCo	Samarium-cobalt magnets
TBP	Tributyl phosphate
TODGA	Tetraoctyl diglycolamide
USA	United States of America
wt %	Weight percentage
XRD	X-ray diffraction

APPENDIX

Instruments and equipment

ICP-OES/MS

Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) was used for most of the measurements of the concentration of elements in the aqueous solutions, both for aqueous phases after solvent extraction and leachate solutions. The model used was iCAP-6000 ICP-OES. This method is commonly used for the analysis of trace metals at ppm levels (mg/L). The machine is made up of two parts, the ICP and the optical spectrometer. The liquid sample is carried into the instrument along with Ar as an aerosol (mist), vaporized, ionized and excited by temperatures of 6 000 – 10 000 K. It works on the principle of plasma excitation of the atoms and the detection of emitted light from the relaxation of the excited atoms by the spectrometer. Every element has a unique set of spectral lines and can be detected individually in a sample.

Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) was used for some measurements of the leachate solutions and aqueous solutions after solvent extraction where the concentrations were in the ppb range ($\mu\text{g/L}$). The model used was iCAP-Q ICP-MS. It consists of two parts, just like the ICP-OES, but instead of an optical emission spectrometer the ICP-MS has a mass spectrometer connected to the inductively coupled plasma. It is roughly 1000 times more sensitive than the ICP OES machine, it has higher precision, sensitivity and speed, although there is a higher risk of interferences and contamination.

SEM/EDX

Scanning electron microscope (SEM) is a type of microscope that creates the image of a surface by scanning it with a focused beam of electrons. The signals that are used to produce an image are a result of the interaction of the beam of electrons with the atoms on the surface and within the material. They are divided into secondary electrons, backscattered electrons and x-rays and give information about the morphology of the sample. Each element has a unique set of peaks on the emission spectrum (characteristic x-rays from specimen), which helps characterize specific elements in the sample. This is the principle on which energy dispersive x-ray spectroscopy (EDX) is based.

Mixer-settlers

Mixer-settlers are used on a large-scale in solvent extraction for achieving high purity metals out of leachate liquors. They are made up of a series of mixer-settler units, like the one presented in Figure 11.1 (a). Normally, the process is run on a counter-current basis (Figure 11.1 (b)) where the organic and the aqueous phase flow in opposite directions. The unit is made up of a mixer compartment, where the aqueous and organic phase are mixed using a stirrer, and the settling compartment, which is where the two phases are separated.

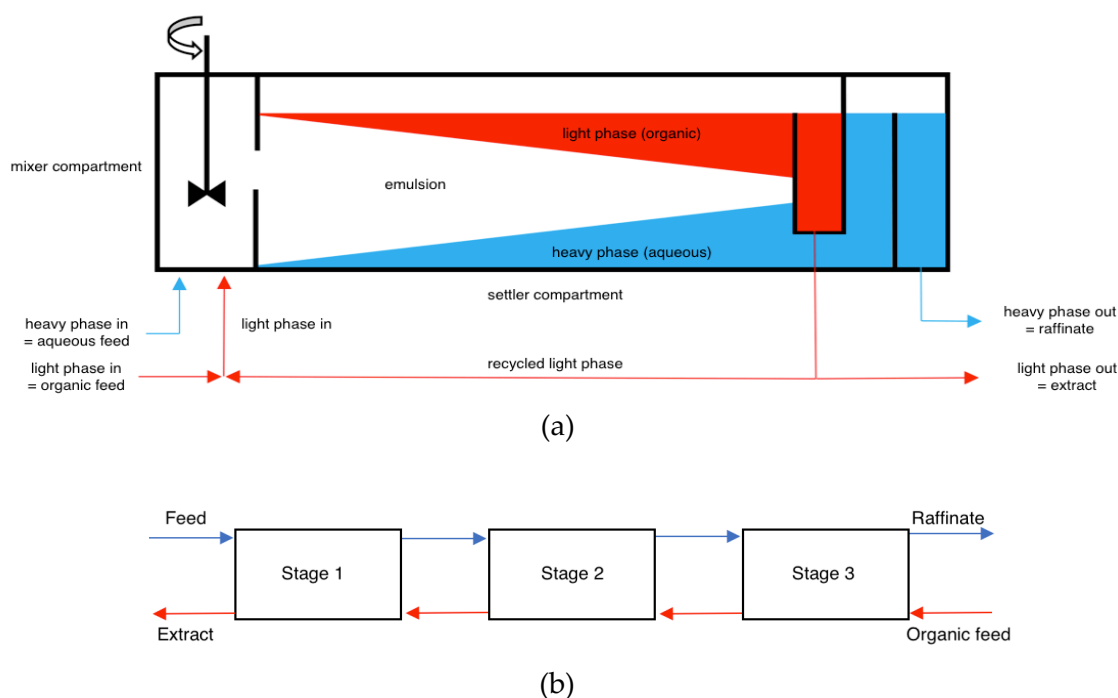


Figure 11.1. Schematic representation of a mixer-settler unit.

Multiple stages are usually needed to achieve high purity metals. This can vary from a few stages up to even 100 for separating adjacent REEs.

The mixer-settlers have a lot of advantages over other processes used in large-scale solvent extraction. They are easy to construct, easy to scale up, not costly, it is easy to predict the number of stages needed, easy to start and restart, and the phase contact is good. On the other hand, some disadvantages of using mixer-settlers on a large scale are requirements for large ground area, large amounts of organic and aqueous phases used and thus large amounts of waste produced, long time to achieve steady state and rather high energy consumption.